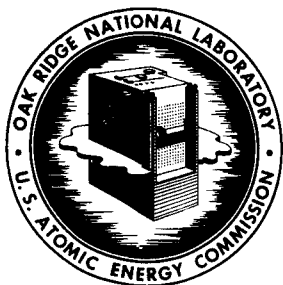# OAK RIDGE NATIONAL LABORATORY

operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

ORNL- TM- 978
NASA CR-54214

AN EVALUATION OF THE CHEMICAL PROBLEMS

ASSOCIATED WITH THE AQUEOUS SYSTEMS IN THE

TUNGSTEN WATER MODERATED REACTOR, ADDENDA 1 AND 2

G. H. Jenks
E. G. Bohlmann
J. C. Griess

CLASSIFICATION CHANGE

TO = UNCLASSIFIED

By authority of T.D. No 74-73

Changed by ____ Date 11/15/73

NOTICE This document contains information of a preliminary nature
and ... Oak Ridge National
Labor...
present a final report.

ORNL-TM-978
NASA CR-54214

AN EVALUATION OF THE CHEMICAL PROBLEMS
ASSOCIATED WITH THE AQUEOUS SYSTEMS IN THE
TUNGSTEN WATER MODERATED REACTOR, ADDENDA 1 AND 2

G. H. Jenks
E. G. Bohlmann
J. C. Griess

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

MARCH 1965

iii

TABLE OF CONTENTS

ADDENDUM 1

NOMENCLATURE

A — Rate of direct formation of H_2 or D_2 in radiolysis of H_2O or D_2O, moles, ℓ^{-1}, sec^{-1}.

B — Rate of direct formation of OH or OD in radiolysis of H_2O or D_2O, moles, ℓ^{-1}, sec^{-1}.

C — Rate of direct formation of H_2O_2 or D_2O_2 in radiolysis of H_2O or D_2O, moles, ℓ^{-1}, sec^{-1}.

F — Rate of direct formation of e_{aq}^- in radiolysis of H_2O or D_2O, moles, ℓ^{-1}, sec^{-1}.

F_{eff} — Effective rate of formation of e_{aq}^- as used in Eq. 10, p. 18.

I — Rate of absorption of radiation energy, w/cc.

K, K', K_1 and K_2 — Constants defined in text.

K'' — Ratio of pressure of H_2 or D_2 to that of O_2 in autoclave with gas space.

L — Rate of direct formation of HO_2 or DO_2 in radiolysis of H_2O or D_2O, moles, ℓ^{-1}, sec^{-1}.

LITR — Low Intensity Test Reactor.

M — Signifies molar. Also used as an abbreviation of moles in expressions of units such as M, ℓ^{-1}, sec^{-1} and sec^{-1}, M^{-1}, ℓ.

(P) — Summation of concentrations of radiolytic products of water, M.

$(P)_{ss}$ — Summation of steady-state concentrations of radiolytic products of water, M.

P — Pressure.

P' — Pressure of gas prevailing in autoclave with gas space, psi.

R — Gas constant — 1.21 psi, ℓ, $mole^{-1}$, $°K^{-1}$.

S^{+n} — Designates oxidized form of solute cation.

$S^{+(n-1)}$ — Product of addition of one electron to oxidized form of solute cation.

T — Temperature, $°K$.

V_g — Volume of gas space in autoclave, ℓ.

V_ℓ — Volume of liquid in autoclave, ℓ.

a — Concentration of solute, M.

α — Concentration of excess oxidant (H_2O_2 or $1/2\ O_2$), M.

$-\alpha$ — Concentration of excess hydrogen, M.

An Evaluation of The Chemical Problems
Associated With The Aqueous Systems in The
Tungsten Water Moderated Reactor, Addendum 1.

G. H. Jenks, E. G. Bohlmann, and J. C. Griess

I. Introduction

Additional considerations have been made of methods of predicting the effects and extent of radiolysis of water and solutions in the TWMR from experimental data which might be obtained at much lower intensities in existing reactors. The work has included consideration of: (1) experimental and theoretical information on the relationship between intensity, I, and concentrations of radiolytic products, $(P)_{ss}$, in pure water, (2) reactions which might occur in solutions under irradiation and the effects of these reactions on the relationship between I and $(P)_{ss}$, and on the relationship between I and factors which might affect the stability of the solution, (3) the relationships between radiolytic behavior of solutions and water caused by fast electrons and by reactor radiations, and (4) feasible experiments which would yield information from which the behavior of solutions under irradiation in the TWMR could be predicted. Calculations employing a revised computer-code were made to determine the relationship between I and radiolytic behavior for certain assumed conditions. The results of these were then used as bases for estimating behavior under other assumed conditions. Considerations of radiolysis under fast electron irradiation were made in order to determine whether the results of feasible Van de Graaff experiments at intensities ranging up to those which will prevail in the TWMR could be used to establish the relationship between I and $(P)_{ss}$

and between I and solution stability during reactor irradiations.

This additional work was prompted initially by the need to have a clearer understanding of how data obtained in low-intensity reactor experiments, such as those suggested previously,[1] would be employed in determining the extent of water decomposition at TWMR intensities, and by a desire to learn whether experimental information on water decomposition obtained at two or more intensities in reactors could be extrapolated directly to TWMR intensities. However, some possible, but previously unrecognized, aspects of radiolysis of solutions have substantially influenced the direction of the work. In particular, it has been recognized that if certain likely combinations of rate constants for the reduction and oxidation of solute-cations prevail, a large fraction of the cations will be in the reduced form at the steady-state. Since the presence of reduced material may affect the extent of solvent decomposition as well as the solution stability, as will be discussed later, it has been necessary to consider methods of testing the effects of reduced solute and of predicting the effects at TWMR intensities. For reasons which will be presented later, circulating loop experiments of the type suggested previously[1] are not suitable for studying radiolysis of solutions in which substantial reduction may occur.

The purpose of this addendum is to present the results of this additional work.

II. Calculations

The computer code described previously[2] was modified to include reactions 24 and 25.

24. $e^-_{aq} + S^{+n} \longrightarrow S^{+(n-1)}$

25. $OH + S^{+(n-1)} \longrightarrow S^{+n} + OH^-$
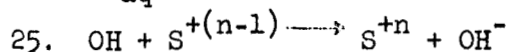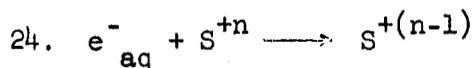
where S^{+n} represents the solute species included in the initial solution (Sm^{+3}, Gd^{+3}, Cd^{+2}, H_3BO_3) and $S^{+(n-1)}$ represents the reduced form of this species. These reactions were included by adding terms to the appropriate equations expressing the equality of rates of formation and disappearance of a radiolytic species[*] as shown in the following:

(5b) $\dfrac{d(e^-_{aq})}{dt} = 0 = X - ak_{24}(e^-_{aq})_{ss}\left(1 - \dfrac{k_{24}(e^-_{aq})_{ss}}{k_{24}(e^-_{aq})_{ss} + k_{25}(OH)_{ss}}\right)$

(1b) $\dfrac{d(OH)}{dt} = 0 = Y - ak_{25}(OH)_{ss}\dfrac{k_{24}(e^-_{aq})_{ss}}{k_{24}(e^-_{aq})_{ss} + k_{25}(OH)_{ss}}$

(7b) $2(H_2)_{ss} + (e^-_{aq})_{ss} + (H)_{ss} + \dfrac{ak_{24}(e^-_{aq})_{ss}}{k_{24}(e^-_{aq})_{ss} + k_{25}(OH)_{ss}} + 2\alpha =$

$$2(H_2O_2)_{ss} + 4(O_2)_{ss} + 3(HO_2)_{ss} + (OH)_{ss}$$

where, a, is the concentration of solute-cations, $(S^{+n})_{ss} + (S^{+(n-1)})_{ss}$, X and Y represent the terms in these equations as written previously, and k_{24} and k_{25} are the rate constants for reactions 24 and 25. Eq. 7b is the material balance equation and has been modified to include the concentration of reduced solute. Terms for the concentrations of the radicals e^-_{aq}, H, and OH were also added to make the equation complete. It may be noticed that the formation of an appreciable concentration of reduced species, $((S^{+(n-1)})_{ss}$ equal to $ak_{24}(e^-_{aq})_{ss}/(k_{24}(e^-_{aq})_{ss} + k_{25}(OH)_{ss})$ has the same effect on the material balance equation as the introduction of excess oxidant at a concentration equal to $0.5(S^{+(n-1)})_{ss}$.

---

[*]See Appendix 1.

All of the previously[2] employed equations and reactions involved are listed in Table 1. Eqs. 5b, 1b, and 7b are revisions of Eqs. 5, 1, and 7 of Table 1.

Rate constants for $90°C$, estimated previously[2] for all reactions except 24 and 25, were used in all calculations. The values used for rates of production of radiolytic species are listed in Tables 2 and 3. The electron-radiation values were based on an LET-value of 0.02 ev per $\overset{\circ}{A}$ and G-values used previously[1] for this LET. The reactor values were based on: (1) an assumed ratio of 2 for the energy deposition rates from neutrons and γ-rays, (2) assumed LET-values of 8.5 and 0.02 ev per $\overset{\circ}{A}$ for neutrons and γ-rays, respectively, and (3) G-values used previously[1] for radiations with these LET-values.

In one portion of the work reported here, it was of interest to extrapolate experimental data at a temperature of $36°C$ to a temperature of $90°C$. The information illustrated in Fig. 1 was employed for this extrapolation. The upper curve represents calculated values for the $(H_2)_{ss}$ in the HFIR core at several temperatures. These values were calculated using a computer code and estimated activation energies for rate constants as reported previously.[2] The points falling near the lower curve are those reported by Hochanadel[3] for the pressures observed in a capsule of water in the ORNL graphite pile at several temperatures. The dotted curve is drawn parallel to the upper curve. There is substantial agreement between the calculated and experimental values for relative pressures at different temperatures.

III. Relationship Between $(P)_{ss}$ and I in Water.

A. Calculated Values

Calculated values for the steady-state concentrations of radiolytic products in pure water under exposure to reactor radiations and to electrons at several intensities are listed in Tables 4 and 5. The $(H_2)_{ss}$ values are plotted vs the square-root of intensity in Fig. 2. For each type of radiation the points fall near a straight line represented by the equation,

$$(1) \quad (H_2)_{ss} = KI^{1/2},$$

where K is a constant for a given type of radiation.

The (H^+) was assumed to be zero for the electron calculations and 10^{-5}M for the reactor calculations. Since the only reaction for H^+ included in the code is the reaction with e^-_{aq} and since the rate constants for reaction of H_2O_2, O_2, and H^+ with this radical are approximately equal, it was assumed that the effect of the H^+ was negligible in the reactor calculations even at the lowest intensity $((H_2)_{ss}$ equal about 10^{-4}M). This assumption was verified by the results of one calculation for 2.5 w/cc in which it was assumed that (H^+) equaled 0.0. As shown in Table 4, the calculated $(H_2)_{ss}$ in this case was 2.17×10^{-4}M compared with the value of 2.23×10^{-4}M found when (H^+) was 10^{-5}M. With electron irradiations, for which $(H_2)_{ss}$ values were near 10^{-5}M, the low (H^+) is more important as will be illustrated in a following paragraph. The slight deviations of the calculated values from a straight line are probably the result of small deviations from strict proportionality between the assumed rates of production of radiolytic species and I.

B. Discussion

Ghormley[4] and Schwarz[5] have demonstrated experimentally that the steady-state concentrations of H_2, O_2, and H_2O_2 produced in pure H_2O by absorption of electron energy increase as the square-root of the rate of energy absorption. That is, the relationship between concentration and power density is of the general form of Eq. 1. Maximum power densities of about 1 and 15 w/cc were employed by the respective investigators. Temperatures were near room temperature. Schwarz[5] has argued that a square-root relationship of the form of Eq. 1 prevails for all the radiolytic species when the equations expressing equality between rates of formation and destruction of radiolytic species are of the general form illustrated in Eq. 2, and when the excess oxidant concentration is zero.

$$(2) \quad G_{H_2} I = k_{12}(OH)_{ss}(H_2)_{ss}$$

In pure water, the equations deduced from the known reactions are of the form of Eq. 2, and Schwarz argued[5] that a square-root relationship is expected to prevail. The calculations made with the computer code, in which the assumed reactions for pure water are also of the form of Eq. 2, confirm the square-root relationship for reactor radiations and electrons. Accordingly, the square-root relationship of Eq. 1 is believed to be well established for pure water. A relationship of the same form will prevail for D_2O, but the value of K will differ somewhat from that for H_2O since the relative and absolute yields of radiolytic species differ somewhat between H_2O and D_2O.

IV. Estimation of $(H_2)_{ss}$ in Pure-Water Moderator of TWMR.

As previously reported[1] and as shown again in Fig. 2, the $(H_2)_{ss}$ at 150 w/cc of reactor radiations determined from estimated rate constants and G-values is 1.7×10^{-3}M ($\sim$ 35 psi) at $90°$C. Now that the square-root relationship is firmly established we are able to provide additional evidence in support of this calculated value. Allen and co-workers[6] measured a $(H_2)_{ss}$ of about 3×10^{-5}M in pure water in capsule experiments in the ORNL graphite reactor where a ratio of 2 prevailed for neutron to γ-ray energy deposition rates.[7] The power density[7] was about 5×10^{-3} w/cc and the temperature was presumably[3] about $35°$C. Extrapolation of these results to 150 w/cc on the basis of a square-root relationship leads to a value of 5.2×10^{-3}M H_2 at $35°$C. Adjustment of these extrapolated values to $90°$C on the basis of the information in Fig. 1 leads to values illustrated in Fig. 3. As can be seen, these extrapolated values differ from those estimated by computer-calculations by a factor of only 1.7. This is considered to be good agreement.

It has been argued previously[1] that the yields of radiolytic products do not change substantially with power density up to 150 w/cc. The validity of this argument is supported by the fact that calculated values for 50 w/cc (1 neutron and 1 γ-ray) in the ETR were in substantial agreement with the experimental values.[1,2] The rate constants are the only other parameters affecting steady-state concentrations in pure water, and these are not expected to change with intensity.

The situation with respect to expected $(H_2)_{ss}$ in the TWMR moderator when the water is pure may now be summarized as follows: The

$(H_2)_{ss}$ may confidently be expected to be below the tolerable limit of about 3×10^{-3}M unless the radiolytic yields change substantially upon increasing the power density from about 50 to 150 w/cc. Experiments in existing reactors will not provide any additional information on the effects of power density or yields since the maximum reactor intensities available for experimentation are thought to be in the range of 15 to 20 w/cc. Additional information on the I vs yields would be obtained in experiments employing fast electrons at intensities up to 150 w/cc as proposed in later paragraphs. Information will also be forthcoming from the HFIR which will operate at a maximum of 100 w/cc in the moderator. An in-pile experiment with H_2O and/or D_2O in which the ratio of neutron to γ-ray energy deposition rates in H_2O is 2 and the temperature is 90°C will be needed as part of the investigation of radiolysis in poison-control solutions as discussed in later paragraphs. This experiment could presumably be carried out at LITR intensities (0.5 w/cc).

It may be noted that the radiolysis of the moderator can be suppressed by the addition of excess H^+ or H_2 or both. Also, the addition of radical scavengers at a concentration of 10^{-5}M or less will probably not increase $(H_2)_{ss}$ above the tolerable level. These factors are discussed in following paragraphs.

V. Estimation of $(H_2)_{ss}$ in Water Containing Excess H_2 and Exposed to Reactor Radiations.

The results of calculations of $(H_2)_{ss}$ in water containing excess H_2 are illustrated in Fig. 4. The calculated concentrations of all radiolytic species are listed in Table 4. The excess (H_2) is given in

the figure and table by the negative value of α.

Substantial reductions in the extent of radiolysis and in the $(H_2)_{ss}$ can be accomplished by the addition of excess H_2. The optimum concentration is apparently near $5 \times 10^{-4}M$ where the expected $(H_2)_{ss}$ and $(H_2O_2)_{ss}$ at 150 w/cc of reactor radiations are $5.5 \times 10^{-4}M$ and $5 \times 10^{-5}M$. The $(O_2)_{ss}$ is negligible. It is evident that no further decrease in $(H_2)_{ss}$ with increasing $(H_2)_{excess}$ above $5 \times 10^{-4}M$ is possible.

VI. Estimation of $(H_2)_{ss}$ in Water Containing H^+ at Several Concentrations.

The calculated effects of converting some or most of the e^-_{aq} to H by the addition of H^+ to water are illustrated in Fig. 5. The calculations for reactor radiations show, somewhat surprisingly, that the conversion of a substantial fraction of e^-_{aq} to H produces a substantial decrease in $(H_2)_{ss}$. It was anticipated that because of the relatively low rate constant for reaction of H with H_2O_2 to produce OH, the conversion would result in higher values of $(H_2)_{ss}$. However, the results showed that the conversion also resulted in a lowered ratio of $(O_2)_{ss}$ to $(H_2O_2)_{ss}$ and a lowered concentration of $(HO_2)_{ss}$. These changes indicate that the importance of the chain reaction which includes HO_2 formation and which leads to the removal of radicals was reduced by the conversion. In the case of the electron irradiations the conversion of a fraction of the e^-_{aq} to H resulted, as expected, in a marked increase in $(H_2)_{ss}$. It is not known whether a higher (H^+) would produce a beneficial effect under electron irradiation.

It may be noted that the concentrations of radiolytic species in solutions containing an appreciable (H^+) do not follow an equation of the form of Eq. 1. This is not surprising since the reaction of e^-_{aq} with H^+ at a constant concentration is not of the general form of Eq. 2.

It should also be noted that one effect of the addition of H^+ will be to repress the ionization of HO_2 and thereby decrease the rate of interactions of HO_2 to form H_2O_2 and O_2. This change may alter the calculated effects of acidification on $(H_2)_{ss}$. Additional calculations and experiments are required to determine the actual effects of acid on $(H_2)_{ss}$.

VII. Reactions in Poison Control Solution Under Irradiation.

In considerations of the radiolysis of the poison control solutions it is necessary to include reactions which are known or which can be postulated to occur between the radiolytic products of water and the solutes. Reactions of probable importance are listed in Table 6 and discussed in subsequent paragraphs. Other reactions which are less likely to be of importance are listed in Table 7.

A. Reducing Reaction

The cations, Sm^{+3}, Gd^{+3}, Cd^{+2}, and H_3BO_3 are known to react with e^-_{aq} and the rate constants for the ions but not for H_3BO_3 have been reported. The reaction with H_3BO_3 is thought to be of the dissociative capture type,[10] primarily, since sodium tetraborate does not react with e^-_{aq}[8] (It should be noted, however, that sodium tetraborate may react with OH[8]). The reactions with Sm, Gd, and Cd are very likely of the nondissociative capture[10] type.

The standard oxidation potential for Sm^{+3}-Sm^{+2} indicates a possibility that Sm^{+3} may be reduced by H. Cadmium is not reduced by H,[11] and it is here considered unlikely that Gd^{+3} or H_3BO_3 are reduced by H.

B. Oxidizing Reactions

The species formed by reaction of Sm, Gd or Cd with e^-_{aq} may be re-oxidized by reaction with one or more different radiolytic species or with H^+. The latter reaction (No. 38) may not occur with Sm II.

Reaction 25 - The reaction with OH is designated as a radical-scavenger reaction because the combination of this and the reduction reaction leads to the removal of a radical pair, e^-_{aq}-OH.

Reaction 35 - Reactions of the reduced species with H is also a scavenger reaction because this reaction results in the formation of H_2 from reaction of e^-_{aq} and H.

Reaction 36 - Reaction of the reduced species with H_2O_2 leads to the formation of OH. This product would also have been formed if e^-_{aq} reacted directly with H_2O_2. Hence, no scavenger action results from reaction 36.

Reaction 37 - Reaction of the HO_2 with the reduced species probably does not effect any scavenger action and may be somewhat beneficial. These tentative conclusions are based on the consideration that HO_2 is formed in reactions that are not directly associated with the presence of the solute, and that, normally, much of the HO_2 reacts with OH to form H_2O and O_2 (reactions 18 and 18b). That is, the HO_2 normally takes part in a chain reaction which results in the formation of H_2O

from H and OH or e^-_{aq} and OH without recombination of any of the molecular products of radiolysis. The removal of HO_2 in reaction 37 would tend to break this chain.

Reaction 38 - Reactions of reduced species with H^+ to form H would not effect a scavenger action.

Rate Constants - The rate constants for these possible oxidizing reactions are unknown. Rate constants for analogous reactions in which other ions are oxidized are known and are included in Table 6. Considerations of the rates for these other reactions suggest that reactions 25 and 35 will be fast, and that reactions 36 and 37 will be much slower. No rate constants for reactions analogous to reaction 38 have been found in the literature, but considering the fact that two positively charged ions react it seems likely that the rate of reaction will be slow.

C. H_2SO_4 Reactions

It has been reported that HSO_4^- reacts with OH and the rate constant has been given as shown for reaction 39. It is likely that the oxidized species will react rapidly with e^-_{aq}, H and $S^{+(n-1)}$ to effect the combination of OH with a reducing radical and thus effect a scavenger action.

VIII. Effects of Reactions 24 and 25 on Radiolysis of Poison-Control Solutions.

As discussed in the preceding section (VII), it is established that most of the solutes which have been suggested for poison-control

solutions will be reduced by e^-_{aq}. The reduced Sm, Gd, and Cd will probably be re-oxidized in one or more of the reactions listed in Table 3. (Reaction 24 as used in this discussion symbolizes reaction 31, 32 or 33). Possible results of such reactions which are of concern are: (1) an increase in the steady-state concentrations of molecular products of water due to preponderance of those oxidizing reactions in which radicals are destroyed (scavenged), and (2) the formation of an appreciable steady-state concentration of reduced species, $(S^{+(n-1)})_{ss}$, due to relatively low rates of re-oxidation. The formation of appreciable $(S^{+(n-1)})_{ss}$ is of concern for several reasons: (1) The solution stability may be affected. For example, the +2 rare earth sulfates may be very insoluble[16] and thus might precipitate. In the case of cadmium, the precipitation of Cd metal from $CdSO_4$ solutions under electron irradiation has been observed experimentally,[11] (2) An effective concentration of excess oxidant equal to $0.5(S^{+(n-1)})$ would be formed, and this would increase the extent of decomposition of water even in the absence of a scavenger effect, and (3) The experimental requirements for investigating solution radiolysis would be affected as discussed in later paragraphs.

In order to provide some bases for estimating the extent of such effects in TWMR solutions and to aid in the design of experiments to determine radiolytic behavior at TWMR conditions, computer calculations were made of steady-state concentrations for a variety of assumed values of a, k_{24}, k_{25}, I and α. Electron as well as reactor radiations were employed in the calculations. Most of the results are listed in Tables 8-12. Values of $(H_2)_{ss}$ are plotted vs $I^{1/2}$ in Figs. 6-9. The results

show that in the presence of the postulated scavenger action, the $(H_2)_{ss}$

and $(H_2O_2)_{ss}$ are appreciably greater than those prevailing in pure water

at the same intensities. However, the ratio of $(H_2)_{ss}$ or $(H_2O_2)_{ss}$ in

the scavenger solution to that in pure water is not constant but

decreases with increasing I. The values of the ratio at 150 w/cc of

reactor radiations for the two different sets of rate constants are

about 2 and 2.7 compared with values of 14 and 22 at 0.5 w/cc (Fig. 6).

To a rough approximation, the calculated value of $(H_2)_{ss}$ in scavenger

solutions can be expressed by Eq. 3.

$$(3) \quad (H_2)_{ss} = K_1 + KI^{1/2}$$

where K is the same constant as that appearing in Eq. 1 and K_1 is a

constant for given values of k_{24}, k_{25}, a, and for a given type of

radiation. As stated previously the value of K is also dependent on

the type of radiation.

The $(H_2O_2)_{ss}$ is approximately equal to $(H_2)_{ss}$ with reactor radi-

ations, that is, $(O_2)_{ss}$ is negligible. However, under electron ir-

radiation, $(O_2)_{ss}$ is appreciable. The relationship between the concen-

trations of radicals and I in scavenger solutions is not the same as

that for $(H_2)_{ss}$ or $(H_2O_2)_{ss}$. This may be seen by considering the

relationship for $(OH)_{ss}$. To a close approximation $(OH)_{ss}$ is given by

Eq. 4 which is derived from reaction 12, (Table 6 of ref. 1).

$$(4) \quad (OH)_{ss} = \frac{A}{k_{12}(H_2)_{ss}},$$

where A is the rate of direct formation of H_2 in radiolysis. Sub-

stituting K_2I for A and substituting from Eq. 3 for $(H_2)_{ss}$ we have

$$(5) \quad (OH)_{ss} = \frac{K_2 I}{k_{12}(K_1 + KI^{1/2})}$$

It may also be shown that the ratio of calculated $(H_2O_2)_{ss}$ to $(OH)_{ss}$ is expressed roughly by Eq. 6 for reactor exposures,

$$(6) \quad \frac{(H_2O_2)_{ss}}{(OH)_{ss}} = \frac{k_{12}}{k_2} \left(K^2 + \frac{2K_1 K}{I^{1/2}} + \frac{K_1^2}{I} \right),$$

and thus the value of the ratio decreases with increasing I as may be seen also by consulting the tabulated results of calculations. Although Eq. 6 cannot be considered applicable for electron irradiation because $(H_2O_2)_{ss}$ cannot be assumed equal to $(H_2)_{ss}$, the results of the calculations show that the value of $\frac{(H_2O_2)_{ss}}{(OH)_{ss}}$ decreases with increasing I by amounts comparable to those found with reactor radiations.

Appreciable concentrations of $S^{+(n-1)}$ are formed with k_{24} and k_{25} equal to 4.7×10^{10} and 3.7×10^{8} sec^{-1},M^{-1},ℓ. However, very low concentrations were found with k_{24} and k_{25} equal to 2.2×10^{9} and 4.7×10^{10}. The values of $(S^{+(n-1)})_{ss}$ do not change appreciably with intensity of reactor radiations for either set of rate constants. Under electron irradiation, a somewhat greater change in $(S^{+(n-1)})_{ss}$ occurs with changing intensity.

Excess H_2 may be very effective in reducing $(H_2)_{ss}$ in scavenger solution as may be seen in Figs. 8 and 9.

Additional understanding of the factors governing radiolysis in scavenger solutions was gained from considerations of relationships discussed in following paragraphs.

It has already been stated that, in pure water, the value of K in

Eq. 1 is dependent upon the type of radiation employed.

$$(1) \quad (H_2)_{ss} = KI^{1/2}$$

This dependence results from the difference between the ratio of radical to molecular product yields for the different types of radiations. For electron radiations where the ratio of $G_{e^-_{aq}} + G_{OH}$ to $G_{H_2} + G_{H_2O_2}$ is 4.9 the value of K given by the computer results is $4.6 \times 10^{-6} M, \ell^{-1}$, $(w/cc)^{-1/2}$. The corresponding values for reactor radiations are 1.15 and 1.38×10^{-4}. These values suggest that the proportionalities shown by Eqs. 8 and 9 are approximately valid for these two types of radiations,

$$(8) \quad K \left(\frac{A+C}{B+F}\right)^2 ,$$

$$(9) \quad K \left(\frac{A}{F}\right)^2 ,$$

where A, C, B, and F are the rates of production of H_2, H_2O_2, OH and e^-_{aq}. However, similar comparisons of values of $(H_2)_{ss}$ calculated for radiations in which in one case the ratio of neutron to γ-ray energy deposition rates was unity and in another case was two, indicates a value of about 3.5 for the exponent rather than the value of 2. The destruction of radicals by scavengers produces a reduction in the number of radicals available for catalyzing the formation of water from H_2 and H_2O_2, and may be regarded as producing a reduction in the effective yields of radicals, and thus in the effective values of the ratios shown in Eqs. 8 and 9. The magnitude of the effective change in F produced by scavengers can be estimated readily for the cases employing reactor radiations since the e^-_{aq} reacts principally with H_2O_2 and

S^{+n}. The normal reaction is that with H_2O_2. The effective value of F is that given by Eq. 10.

$$(10) \quad F_{eff} = F - \frac{F k_{24}(S^{+n})_{ss}(e^-_{aq})_{ss}}{k_{24}(S^{+n})_{ss}(e^-_{aq})_{ss} + k_9(H_2O_2)_{ss}(e^-_{aq})_{ss}}$$

The final term is the expression for the rate of reaction of e^-_{aq} with S^{+n}.

Rearranging,

$$(11) \quad \frac{1}{F_{eff}} = \frac{1}{F}\left(\frac{k_{24}(S^{+n})_{ss}}{k_9(H_2O_2)_{ss}} + 1\right)$$

We may now write Eqs. 12 and 13.

$$(12) \quad \left(\frac{A}{F_{eff}}\right)^2 = \left(\frac{A}{F}\right)^2 \left(\frac{k_{24}(S^{+n})_{ss}}{k_9(H_2O_2)_{ss}} + 1\right)^2$$

$$(13) \quad (H_2O_2)_{ss} = K'I^{1/2}\left(\frac{k_{24}(S^{+n})_{ss}}{k_9(H_2O_2)_{ss}} + 1\right)^2$$

Comparison of values calculated from Eq. 13 and by the computer code shows that Eq. 13 is incorrect and that the values of the exponent must be 5 to 6 rather than 2. However, Eq. 13 will serve as a basis for estimating the qualitative effects on $(H_2O_2)_{ss}$ or $(H_2)_{ss}$ of changes in k_{24}, k_{25}, and a.

Eq. 14 is another equation of interest which can be derived by equating rates of formation and disappearance of $S^{+(n-1)}$ and by substituting for $(OH)_{ss}$ from Eq. 4. It was assumed that $(H_2O_2)_{ss}$ equals $(H_2)_{ss}$, and a series expansion of a quadratic equation was employed in the derivation.

$$(14) \quad \frac{a}{(S^{+n})_{ss}} - 1 = \frac{(S^{+(n-1)})_{ss}}{(S^{+n})_{ss}} = \frac{k_{24}}{k_9}\left(\frac{F}{A}\frac{k_{12}}{k_{25}} - \frac{a}{(H_2O_2)_{ss}}\right).$$

The relationships indicated by Eq. 14 are in approximate agreement with the computer results for case 1 (Table 8). However, for case 2 (Table 9), in which the computer calculated values of $(S^{+(n-1)})_{ss}/(S^{+n})_{ss}$ are about 10^{-3}, Eq. 13 fails since the term in parentheses is negative. The inclusion of additional terms in the series expansion might remedy this. This equation is not valid for electron irradiations because the assumption that $(H_2O_2)_{ss}$ equals (H_2) is not valid for these irradiations. In spite of limited validity, Eq. 14 as well as Eq. 13 is of value in estimating effects on radiolysis of changes in various parameters.

A qualitative explanation for the small difference between $(H_2O_2)_{ss}$ at, say, 0.5 and 150 w/cc is evident from Eq. 13. As H_2O_2 increases slightly from the value at 0.5 w/cc, the fraction of e^-_{aq} (or OH) which reacts with H_2O_2 (or H_2) rather than with the scavenger increases so that the effective yield of radicals increases with increasing $(H_2O_2)_{ss}$. If the fraction did not change with increasing $(H_2O_2)_{ss}$ (i.e., with increasing intensity), a square-root relationship of the form of Eq. 1 would prevail.

An increase in the value of k_{24} will effect a substantial increase in $(H_2O_2)_{ss}$ unless $(S^{+n})_{ss}$ decreases proportionally. For case 2, in which the assumed values of k_{24} and k_{25} are 2.2×10^9 and 4.7×10^{10}, a factor of ten increase in the value of k_{24} would probably not decrease $(S^{+n})_{ss}$ appreciably, but would increase $(H_2O_2)_{ss}$. The effects of changes in k_{25} may be thought of as the effects of corresponding changes in $(S^{+n})_{ss}$. For case 2, a reduction of a factor of ten for the assumed value will probably have little effect on $(S^{+n})_{ss}$

although the fractional increase of $(S^{+(n-1)})_{ss}$ is large (see Table 10 for case 3). Hence this postulated change in k_{25} would not affect $(H_2O_2)_{ss}$ appreciably. Change in the value of (a) for case 2 from 0.02M to, say, 0.002 M would reduce $(S^{+n})_{ss}$ by a factor of ten at the least. Accordingly, a marked reduction in $(H_2O_2)_{ss}$ would occur.

For case 1 in which the assumed values of k_{24} and k_{25} are 4.7×10^{10} and 3.7×10^8, a factor of ten decrease in k_{24} would probably increase the value of $(S^{+n})_{ss}$ significantly, and, thus, the effect of this change on $(H_2O_2)_{ss}$ may be small. On the other hand, a change in the value of k_{25} would result in a change of the same direction in $(S^{+n})_{ss}$, and, thus, in $(H_2O_2)_{ss}$. An increase in the value of (a) for case 1 would result in an increase in $(S^{+n})_{ss}$, and, thus, in an increase in $(H_2O_2)_{ss}$.

IX. Possible Importance of Non-Scavenger Reactions.

Assuming that certain rate constants and/or combinations of constants prevail, the non-scavenger-oxidizing reactions may be of importance in the radiolysis and in the design of experiments as discussed more fully in this section.

A. Comparisons Between Reactions 25 and 36

1. Continuous Irradiation.

In order that essentially all of the reduced species reacts with H_2O_2 rather than OH, it may be assumed the ratio of reaction rates must favor the reaction with H_2O_2 by a factor of ten. The following relationship must then prevail.

$$(15) \quad k_{25}(OH)_{ss}(S^{+(n-1)})_{ss} < 0.1 \, k_{36}(H_2O_2)_{ss}(S^{+(n-1)})_{ss}$$

Making the assumption that $(H_2)_{ss}$ equals $(H_2O_2)_{ss}$ and substituting for $(OH)_{ss}$ from Eq. 4 leads to Eq. 16,

$$(16) \quad k_{36} > k_{25}A/0.1 \, k_{12}(H_2O_2)_{ss}^2.$$

Putting in the value for A at 150 w/cc of reactor radiations and setting $(H_2O_2)_{ss}$ equal to the value of 1.7×10^{-3}M calculated for pure water gives, $k_{36} > 1.8 \times 10^{-3} \, k_{25}$. Then, if k_{25} equals, say, 10^9, k_{36} must be greater than 1.8×10^6 sec^{-1},M^{-1},ℓ in order to eliminate the scavenger reaction.

It is interesting to note that Eq. 16 predicts a power density dependence for the required ratio of k_{36} to k_{25} unless $(H_2O_2)_{ss}$ is proportional to $I^{1/2}$. As noted previously (Eq. 3) the rate of increase of $(H_2O_2)_{ss}$ in scavenger solutions is much less than that expected for a square-root dependence. Hence, the required ratio of k_{36} to k_{25} increases with increasing intensity. As a result, the possibility must be recognized that the extent of scavenger action will increase with increasing intensity. The particular case in which no scavenger action occurs at low intensity has not been analyzed completely by computation but it is very likely that the ratio of $(H_2O_2)_{ss}$ to $(OH)_{ss}$ is independent of I in this case. Accordingly, no change in scavenger action with increasing intensity is expected in this case.

2. Intermittent Irradiation.

For systems in which the solution is intermittently exposed to radiation, reaction 36 may be of importance even though k_{36} is so low

that it is not important in comparison with reaction 25 during irradiation. For example, assume that k_{36} equals 10^3 and $(H_2O_2)_{ss}$ equals $3 \times 10^{-3}M$. The rate of destruction of $S^{+(n-1)}$ after irradiation is expressed by Eq. 17 if it is assumed that (H_2O_2) does not change appreciably during the reaction of $S^{+(n-1)}$ with H_2O_2.

$$(17) \quad \frac{d(S^{+(n-1)})}{dt} = -2k_{36}(H_2O_2)_{ss}(S^{+(n-1)})$$

Integrating and substituting values for k_{36} and $(H_2O_2)_{ss}$

$$(18) \quad \frac{(S^{+(n-1)}}{(S^{+(n-1)})_o} = e^{-6t}$$

Equation 18 shows that the $(S^{+(n-1)})$ is reduced rapidly under these assumed conditions; for example, to 5 per cent of the initial value in 0.5 sec. The importance of this consideration is that the maximum concentrations of $S^{+(n-1)}$ which are recorded during intermittent irradiations at low intensities may be appreciably less than those which would prevail during continuous irradiations at the same intensities. If this is the case it is probable that the concentrations of other radiolytic species would also differ from the one irradiation procedure to the other. In our considerations of relationships between radiolytic behavior and exposure parameters, it has been assumed that steady-states are reached which are representative of those prevailing during continuous exposure. We do not understand how to employ results such as might be obtained in intermittent irradiation experiments in these considerations.

B. Comparisons Between Reactions 25 and 37

1. Continuous Irradiation.

Making assumptions analogous to those for reaction 36, Eq. 19 must prevail in order to suppress reaction 25,

$$(19) \quad k_{25}(OH)_{ss}(S^{+(n-1)})_{ss} < 0.1 \, k_{37}(HO_2)_{ss}(S^{+(n-1)})_{ss},$$

and Eq. 20 is obtained from Eq. 19.

$$(20) \quad k_{37} > \frac{k_{25}}{0.1} \, \frac{A}{k_{12}(H_2O_2)_{ss}(HO_2)_{ss}} .$$

Substituting the value for A at 150 w/cc of reactor radiations, setting $(H_2O_2)_{ss}$ equal to $1.7 \times 10^{-3}M$, and assuming that $(HO_2)_{ss}$ is $10^{-5}M$, (i.e., near the maximum value calculated for $(HO_2)_{ss}$) gives, $k_{37} > 3.2 \times 10^{-2} k_{25}$. In practice, if reaction 37 does occur importantly, the $(HO_2)_{ss}$ would probably be less than $10^{-5}M$, but there is no way of simply estimating the actual concentration.

It should be noted that the pKa of HO_2 is about 4.4 so that the pH of the solution must be below about 4 in order that the full concentration of HO_2 be available for reaction 37. The reaction of $S^{+(n-1)}$ with O_2^- is probably much slower than with HO_2.

The results of the calculations show that the ratio $(HO_2)_{ss}/(OH)_{ss}$ decreases with increasing intensity in scavenger solutions. Hence, the value of ratio of k_{37} to k_{25} required to suppress reaction 25 probably increases with increasing intensity. The significance of this with respect to expected changes in extent of scavenger effects with changing intensity is analogous to that discussed above for reaction 36.

2. Intermittent Irradiation.

The expected maximum $(HO_2)_{ss}$ of about $10^{-5}M$ is insufficient to

effect significant changes in $S^{+(n-1)}$ after irradiation. Therefore, no difference is expected between continuous and intermittent irradiations if reaction 37 predominates.

C. Comparisons Between Reactions 25 and 38.

1. Continuous Irradiation.

Making assumptions analogous to those for reaction 36, Eq. 21 must prevail in order to suppress reaction 25,

$$(21) \quad k_{25}(OH)_{ss}(S^{+(n-1)})_{ss} < 0.1 \; k_{38}(H^+)(S^{+(n-1)})_{ss},$$

and Eq. 22 is obtained from Eq. 21,

$$(22) \quad k_{38} > \frac{k_{25}}{0.1} \; \frac{A}{k_{12}(H_2O_2)(H^+)} \; .$$

Again setting A at the value for 150 w/cc of reactor radiations, setting $(H_2O_2)_{ss}$ equal to $1.7 \times 10^{-3}M$, and assuming that (H^+) equals $10^{-3}M$ gives, $k_{38} > 3.6 \times 10^{-4} \; k_{25}$. This relationship is, of course, expected to change in direct proportion to changes in (H^+). It may be noted that $S^{+(n-1)}$ and H^+ are produced in equivalent amounts under irradiation so that if (H^+) is low initially, it may become appreciably higher during irradiation.

The ratio of $(H^+)_{ss}/(OH)_{ss}$ decreases with increasing intensity. Accordingly, the relative importance of the scavenger reaction 25 increases with increasing intensity.

2. Intermittent Irradiation.

On the bases of considerations analogous to those discussed for reaction 36, it is apparent that reaction 38 may produce important changes in solution during short intervals between irradiations even

though the reaction is unimportant during irradiations. Therefore, the results of experiments employing continuous irradiation may differ from those in which irradiation is intermittent.

D. Formation of $S^{+(n-1)}$ with Non-Scavenger Reactions

The possibility of appreciable $(S^{+(n-1)})_{ss}$ formation exists when non-scavenger reactions are important just as it does when the scavenger reaction (reaction 25) predominate. The probability of appreciable $(S^{+(n-1)})$ formation is thought to be greatest when scavenger action is least. The belief is based on the consideration that the rates of the non-scavenger reactions are likely to be low compared with the rates of reaction 24.

X. Effects of (H_2SO_4) on Radiolysis of Poison-Control Solutions

A. Effect of (H^+)

As mentioned previously, the conversion of e^-_{aq} to H according to reaction 22 has a beneficial effect on the $(H_2)_{ss}$ in otherwise pure water under exposure to reactor radiations. A much greater beneficial effect can be expected in the poison-control solutions since, with the possible exceptions of Sm^{+3}, the poison-control cations probably do not react with H at appreciable rates. Thus, if the (H^+) is made sufficiently large, all scavenger action and all possibility of appreciable $(S^{+(n-1)})$ formation as well would be eliminated. The (H^+) required can be estimated by assuming that the rate of reaction 22 must exceed that of reaction 24 by a factor of ten in order to suppress the latter reaction. That is,

$$(23) \quad k_{24}(e^-_{aq})(a) < 0.1\, k_{22}(H^+)(e^-_{aq}).$$

The required (H^+) is then,

(24) $(H^+) > 0.1 \dfrac{k_{24} \ a}{k_{22}}$, or

(25) $(H^+) > 1.8 \times 10^{-10} \ k_{24} \ a$ at $90°C$.

Now if k_{24} and (a) equal 5×10^{10} and 3×10^{-3}, the (H^+) must exceed $2.7 \times 10^{-2} M$. (a factor of two-thirds reduction could be obtained at (H^+) equal to $8 \times 10^{-3} M$.) Proportionately higher or lower (H^+) are required as the product $k_{24}(a)$ is increased or decreased.

B. Effect of (HSO_4^-)

As noted in Table 6, HSO_4^- reacts with OH (reaction 39) to initiate a scavenger reaction. Presumably the (HSO_4^-) at which this reaction becomes important should not be exceeded. This permissible (HSO_4^-) can be estimated by assuming that the rate of reaction 39 must not exceed one-tenth the rate of OH reaction with H_2 and H_2O_2.

(26) $k_{39}(OH)_{ss}(HSO_4^-) < 0.1(k_{12}(OH)_{ss}(H_2)_{ss} + k_{14}(OH)_{ss}(H_2O_2)_{ss})$

Introducing values for k_{12}, k_{14} and k_{39}, and assuming $(H_2)_{ss}$ equals $(H_2O_2)_{ss}$,

(27) $(HSO_4^-)_{max} < 11(H_2)_{ss}$ M at $90°C$.

It is apparent that the value of (HSO_4^-) at the permissible limit defined here depends upon the $(H_2)_{ss}$ and $(H_2O_2)_{ss}$ which occur in the absence of a HSO_4^- effect. It is therefore dependent upon the radiation intensity and upon the occurrence of other scavenger action. Thus, in pure water at 0.5 w/cc of reactor radiation, the addition HSO_4^- at a concentration greater than $1.1 \times 10^{-3} M$ will produce some scavenger action. At 150 w/cc the HSO_4^- concentration may be as high as

1.9×10^{-2}M before any appreciable scavenger action occurs. Now if the $(H_2)_{ss}$ equals say 10^{-2}M in any system as the result of action of other scavengers, HSO_4^- may be added at a concentration of 0.11M without producing any additional scavenger action. Turning the argument around, it also seems likely that HSO_4^- at a concentration of 0.11 in otherwise pure water would produce a $(H_2)_{ss}$ of less than 0.01M ($\sim$ 200 psi).

XI. Design of Experiments for TWMR Poison-Control Solutions

A. Effects of Reduced Species on the Design and Objectives of Experiments.

In designing experiments to study radiolysis of the poison-control solutions, it must be recognized that a significant concentration of reduced species may exist during irradiation. The possible presence of the reduced species will affect the design and/or the objectives of the experiments in several ways.

1. Intermittent vs. Continuous Irradiation.

As previously discussed, the reduced species may undergo an appreciable amount of reaction with H_2O_2 or water after irradiations even though these reactions are not important during irradiation in comparison with the reaction between the reduced species and radicals. Accordingly, the steady-state concentrations during continuous and intermittent irradiations may differ. Also, it is likely that the amount of difference will change with I. In order to eliminate uncertainties in the effects of intermittent irradiation on the concentration of the reduced species, and to simulate as nearly as possible the steady-state conditions in the TWMR, it will be necessary to employ

continuous irradiations. A circulating loop experiment of the type proposed previously,[1] or of the type which has been tentatively considered with the ETR-boric acid loop will not be suitable. Of course, if it can be shown that the concentration of reduced species is negligible in a given solution, that solution can then be studied in a circulating loop.

2. Change in Concentration of H_2 After Irradiation.

If an appreciable amount of reduced material is formed, there is a possibility that the concentration of H_2 may change appreciably after irradiation is stopped. This is because radicals (OH and H) are formed in reactions of the reduced species with H_2O_2 and H^+, and these will lead to recombination of H_2 and H_2O_2 through the chain reactions, 12 and 21 (Table 6 of Ref. 1),

12. $OH + H_2 \longrightarrow H_2O + H,$

21. $H + H_2O_2 \longrightarrow H_2O + OH.$
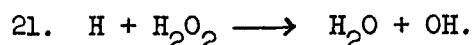
Hydrogen gas may also be formed by reaction of precipitated, reduced, material with water. If the $(H_2)_{ss}$ is to be determined from measurements of hydrogen concentration carried out after irradiation, the measurements must be completed before the concentration changes appreciably from that prevailing during irradiation, or the rate of disappearance at appropriately short delay times must be determined and the results extrapolated to zero time. Order of magnitude estimates of the delay times which would be tolerable under extreme conditions have been estimated as follows:

a. Assume $S^{+(n-1)}$ disappears by reaction with H_2O_2 in reactor

experiments,

$$36. \quad H_2O_2 + S^{+(n-1)} \longrightarrow OH + OH^- + S^{+n} .$$
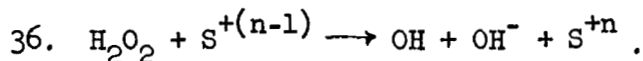
The maximum $(S^{+(n-1)})_{ss}$ which can occur is that given by Eq. 28,

$$(28) \quad (S^{+(n-1)})_{ss} = \frac{F}{k_{36}(H_2O_2)_{ss}} ,$$

where F is the rate of production of e^-_{aq}. Eq. 28 was derived by assuming that all e^-_{aq} react with S^{+n} to form $S^{+(n-1)}$ (that is, that $k_9(H_2O_2)$ is small compared to $k_{24}(S^{+n})$, and that $S^{+(n-1)}$ reacts only with H_2O_2). In practice, the rate of $S^{+(n-1)}$ formation may be smaller, and other reactions of $S^{+(n-1)}$ may be important. In either of these events, the value of $(S^{+(n-1)})_{ss}$ will be less than the value given by Eq. 28. Eq. 29 follows from Eq. 28,

$$(29) \quad k_{36}(H_2O_2)_{ss} = \frac{F}{(S^{+(n-1)})_{ss}} .$$

The change in $(S^{+(n-1)})$ after time (t) following irradiation is given by Eq. 30 if it is assumed that (H_2O_2) does not change appreciably as a result of the reaction 36 or other reactions.

$$(30) \quad \frac{(S^{+(n-1)})}{(S^{+(n-1)})_{ss}} = e^{-k_{36}(H_2O_2)_{ss}t} .$$

Estimates of changes in $S^{+(n-1)}$ based on Eqs. 29 and 30 for several power densities of reactor radiations, and for several assumed values of $(S^{+(n-1)})_{ss}$ and delay times are listed in Table 13. Also listed are values for estimated total and percentage changes in (H_2). Values for total changes in (H_2) were obtained by assuming that each OH led to the reaction of five H_2 to form water. The calculated values of $(H_2)_{ss}$ shown in Fig. 2 were employed in arriving at percentage changes. These

estimates indicate that the results of measurements as a function of delay times of 10^{-2} to 10^{-1} sec will enable evaluations of $(H_2)_{ss}$ at all power densities which are likely to be used in reactor experiments. Because of the extreme conditions assumed in these estimates, it is likely that somewhat larger delay times can also be used.

It may be noted that the actual measurements of (H_2) need not be made at the given delay time. It is only necessary to suppress the reaction between OH and H_2 at the desired time. This can be accomplished by mixing a scavenger for OH into the solution (for example, H_2O_2) or by stripping the H_2 from the solution. The measurements of the amount of H_2 can then be made at any time.

It may also be noted that if the delay time is 10^{-3} sec the difference between (H_2) and $(H_2)_{ss}$ will be negligible.

b. Assume $S^{+(n-1)}$ Disappears by Reaction with H_2O_2 in Van de Graaff Experiments.--Estimates of changes in $(S^{+(n-1)})$ and (H_2) after exposure to Van de Graaff electrons were made by the method described in the preceding paragraphs. The results are listed in Table 14. They indicate that measurements of hydrogen concentration as a function of delay times of 10^{-4} to 10^{-3} sec would be suitable at low intensities. However, at 50 to 150 w/cc it may be necessary to make measurements within 10^{-5} to 10^{-4} sec after irradiation.

c. Assume $S^{+(n-1)}$ Disappears by Reaction with Hydrogen Ion.--If it is assumed that $S^{+(n-1)}$ disappears by reaction with H^+, the maximum $(S^{+(n-1)})_{ss}$ which can occur is given by Eq. 31.

$$(31) \quad (S^{+(n-1)})_{ss} = \frac{F}{k_{38}(H^+)} .$$

The maximum change in $(S^{+(n-1)})$ a given time after irradiation is given by Eq. 32.

$$(32) \quad \frac{(S^{+(n-1)})}{(S^{+(n-1)})_{ss}} = e^{-k_{38}(H^+)t}$$

Eqs. 31 and 32 are analogous to Eqs. 28 and 30, and the results of estimates for reactor radiations and Van de Graaff electrons are the same as those described for the cases in which the $S^{+(n-1)}$ reacts with H_2O_2.

d. Assume Precipitated, Reduced, Material Reacts with Water to Form H_2.--Estimates of the maximum changes in the amount of reduced material which can occur in a given delay period can be made by the methods employed for the H_2O_2 reaction with $S^{+(n-1)}$, and the results are the same as those for the H_2O_2 reaction. However, no chain reaction of the product occurs in this case so that the maximum percentage changes in (H_2) after a given delay period are smaller.

The results of these estimates show that the $(H_2)_{ss}$ in reactor experiments must be measured during exposure to radiation, or the (H_2) must be measured or the reaction affecting (H_2) must be suppressed after delay periods which do not exceed 10^{-2} to 10^{-1} sec. Of course, if it is demonstrated that no change in (H_2) occurs after irradiation, the $(H_2)_{ss}$ can be measured at any time. In the event that H_2 is produced by reaction of precipitated material with water, the reaction cannot be suppressed, and it will be necessary to evaluate the amount of H_2 produced in this way from other information regarding the amount of precipitated material.

For electron irradiations, the results of estimates show that the (H_2) must be measured after delay times which do not exceed 10^{-5} to 10^{-4} sec in high power density experiments, or, alternatively, that the $(H_2)_{ss}$ be measured during exposure.

3. Solution Stability.

Because of the possibility that an appreciable concentration of reduced solute may be formed, there is also a possibility that a solution will be unstable to some extent during irradiation. That is, the reduced material may precipitate on surfaces or form suspended solids faster than precipitated material is redissolved. Loss of solute from the solution by precipitation on surfaces would affect the interpretation of the results of measurements of radiolytic gas pressures, and also affect the usefulness of the solution in the TWMR. Formation of suspended solids would also affect the interpretation of the experimental results but would not necessarily affect the usefulness of the solution if the life-time of suspended solids were sufficiently short. Accordingly, it will be necessary to evaluate the stability of a solution under irradiation as well as the extent of radiolytic decomposition of the solvent.

B. Other Experimental Requirements

Other experimental requirements which may be restated here are: (1) the temperature should be closely controlled since steady-state concentrations are temperature dependent, and (2) the ratio of neutron to γ-energy deposition rates in H_2O in reactor experiments should be the same as that expected in the TWMR if the experimental results are

to be extrapolated to TWMR conditions without benefit of a complete knowledge of radiolytic yields, reactions, and rate constants.

C. Methods of Determining $(H_2)_{ss}$.

As stated previously, the initial experiments must be designed to measure $(H_2)_{ss}$ during irradiation or within a very short period after irradiation. Several methods of determining $(H_2)_{ss}$ at zero or short delay times have been considered.

1. Determinations of $(H_2)_{ss}$ During Irradiation.

a. Measurement of Pressure Above Irradiated Solutions.-One method which has been considered is that of measuring the pressure generated within a gas phase in contact with the irradiated liquid. This method is complicated since any gas space large enough to be useful in measuring equilibrium gas pressures would contain a large fraction of the gas within the system, and the gas would be rich in H_2 since, in general, a majority of oxidant exists as H_2O_2. Excess oxidant would thus be formed in solution and would alter the radiolytic behavior. It is, of course, possible to add H_2 and to vary the ratio of volumes of gas to liquid spaces in order to alter the fraction of H_2 which is in the gas space. However, even with such modifications, it may not be possible to achieve a steady-state in which the concentration of excess oxidant is near a value of interest (α-values ranging from zero to about -2×10^{-3}M are of interest).

Thus, consider a system in which no H_2 is added initially. The relationship between α and other parameters in this system is given by Eq. 33,

$$(33) \quad \alpha V_\ell = \frac{V_g}{RT} \; P' \left(\frac{1-2K''}{1+K''}\right) ,$$

where V_ℓ and V_g are the volumes of liquid and gas spaces in an auto-clave, R is the gas constant $(1.21 \; \frac{\text{psi}, \ell}{\text{mole}, {}^\circ\text{K}})$, K'' is the ratio of the pressure of O_2 to that of H_2, and P' is the observed gas pressure during irradiation. Typical values of K'' given by the results of calculations for reactor radiations are near 0.1 for α near zero. However, the value of K'' probably increases with increasing values of α. Since the value of α increases with increasing P', the increase in pressure may be limited only by the increase in K''. (Radiation induced recombination in the gas phase may also aid in limiting the pressure). The observed pressure in this case is of no interest in this work. Certain experimental results reported by others can be regarded as support for these conclusions (Ref. 6, p. 577).

Now if H_2 is added to the system while the pressure is high, the value of α will decrease, and a condition should be reached, as H_2 is added, in which the pressure starts to decrease as a result of the re-combination of H_2 and oxidant. This decrease will reduce the value of α still further and result in additional recombination of H_2 and oxi-dant. The system is not completely understood and it is not known whether the pressure would decrease to that of the added H_2 or level off at some intermediate value. In the event the latter behavior occurs, it is likely that the α value could be adjusted as desired, and the system would be useful in determining the steady-state concen-trations of radiolysis products. It may be added that the behavior of

the system when H_2 is added initially is also not understood. In this case there is a possibility that, once started, the pressure continues to rise to a value limited by the increase in K''.

Experiments are required to establish the behavior and possible usefulness of this system.

b. Measurement of V vs P In a One-Phase System.--In principle, the vapor pressure of a gas dissolved in solution can be determined by measuring the overpressure at which gas bubbles form in solution. In irradiation experiments, such measurements would be carried out using an autoclave system completely filled with solution and connected to equipment outside of the radiation zone and shields by means of a small tube which would also be filled with solution. An increase in the level of the liquid in the tube as the overpressure is decreased will indicate the formation of gas-vapor bubbles within the autoclave. In practice, the sensitivity of the method will be affected by supersaturation, and the suitability of the method must be established experimentally. It seems likely that a fair degree of accuracy can be achieved in reactor experiments where the expected minimum gas pressure at 0.5 w/cc is about 2 psi. It is less likely that this method would be suitable for use in Van de Graaff experiments where high power densities and vigorous stirring are employed and where the expected minimum pressures range from about 0.2 psi at 4 w/cc to 1 psi at 150 w/cc.

2. Determination of $(H_2)_{ss}$ After Irradiation.

The possibility of determining the steady-state concentration of

H_2 during exposure from the results of measurements carried out after exposure has been mentioned previously. These post-irradiation measurements of H_2 must be accomplished during short delay times, or the possibility of back reaction of H_2 with OH must be eliminated during the short delay times by separating the gas from the solution or by adding a scavenger of OH to the solution. The permissible delay times for Van de Graaff experiments are so short that it seems unlikely that post-irradiation measurements are feasible. The delay times may be greater in reactor experiments (10^{-2} to 10^{-1} sec), and it is likely that provisions can be made for mixing the solution with an OH scavenger within the permissible delay periods. However, further consideration of mixing methods and some experimentation are required to establish the suitability of this method. The separation of the gas from the liquid within short delay times is less likely to prove feasible.

3. Summary

No simple method is available for determining steady-state concentrations of radiolytic gases in solutions. Several methods have been considered which may prove suitable for accomplishing these determinations in reactor experiments. It is believed that the method in which measurements are made of the pressure at which gas bubbles form holds the most promise. Experimental work is required to establish the accuracy which can be achieved with this method or with any of the other methods considered. The methods of determining $(H_2)_{ss}$ from measurements made after irradiations are probably not feasible in Van de Graaff experiments. Also, other methods are less likely to prove

feasible for Van de Graaff than for reactor experiments because of the low concentrations and low solution volumes which will prevail in the former experiments.

D. Methods of Determining Solution Stability

The obvious and most feasible method of determining whether solute is lost from solution is to expel the solution from the autoclave during irradiation and then determine the concentration of the solute in the expelled solution. A fine filter at the entrance to the sample line will retain suspended solids in the autoclave. The sensitivity of this method will be directly proportional to the sensitivity of the chemical analyses. Presumably, sensitivities of about one per cent or better can be achieved.

In-pile as well as Van de Graaff experiments can be equipped to carry out determinations of loss of solute. It may be noted that these stability experiments may be separate from those designed to measure gas concentrations. No gas space will exist in a stability experiment, and expulsion of the solution will be accomplished by compressing the autoclave.

XII. Recommended Experimental Program

Discussion.--The experimental approach which will be required will depend to a large extent upon whether scavenger action or an appreciable concentration of reduced solute or both are expected in the solution of interest. If valid reasons exist for believing that neither scavenger action nor reduced solute occurs in a given solution, the concentration of radiolytic products can be determined in an autoclave experiment in

which the solution is withdrawn and analyzed at a convenient time. A loop can also be employed if this is desirable. The maximum pressure which will occur at TWMR intensities can be confidently predicted from the results of measurements at some low intensity (say 0.5 w/cc in the LITR) using the square-root relationship. In order to add confidence to the predicted values it will be desirable to carry out an experiment at another, higher intensity, (say 5 w/cc in the ORR or 15 w/cc in the ETR). On the other hand, if scavenger action or appreciable reduced solute or both may occur, the experiments must be of the type in which continuous irradiation is employed and $(H_2)_{ss}$ is determined during or shortly after irradiation. The solution stability during irradiation must be determined over a range of power densities up to intensities comparable to those of the TWMR in order to demonstrate that the solution will be suitable in TWMR. Van de Graaff experiments at intensities up to 150 w/cc can be employed for these solution stability studies. Assuming that the solution is stable, it will be necessary to show whether a scavenger action occurs, and, if so, the extent of the scavenger action in in-pile experiments at available intensities (say 0.5 w/cc in the LITR). If no scavenger action occurs, the maximum pressures at TWMR intensities can probably be predicted from the low intensity result using the square-root relationship, but additional computer calculations and, possibly, additional experiments at higher intensities are required to confirm this. If scavenger action occurs, additional computer calculations and, possibly, additional experiments at higher intensities are required to determine the maximum pressure at TWMR intensities. Van de Graaff Experiments to determine

$(H_2)_{ss}$ over a range of intensities up to 150 w/cc would aid greatly in extrapolating the results of low intensity reactor experiments.

There is reason to believe that no scavenger action will occur in certain solutions in which the (H^+) exceeds a value which is dependent upon the rate constant for reduction of solute by e_{aq}^- and upon the concentration of solute. Assuming that separated isotopes are employed, the concentrations of (H^+) required in solutions of $Gd_2(SO_4)_3$ and $CdSO_4$ are about 0.0014 M and 0.3 M. There is reason to believe that boric acid will not be reduced by e_{aq}^- but it may react with OH. The product of the OH reaction would probably react with reducing radicals; thus a scavenger action with H_3BO_3 may occur. $Sm_2(SO_4)_3$ may react with H as well as e_{aq}^- so that additions of H^+ will not necessarily eliminate scavenger action or reduced solute.

A summary of an experimental program for evaluating the stability and gas generation of poison-control solutions in the TWMR is given in Table 15. Most of this summary was developed during a conference attended by H. W. Davison and M. Krasner of Lewis Laboratory and E. G. Bohlmann, J. C. Griess, and G. H. Jenks or ORNL.

Program for Cadmium Sulfate Solution.--It has been decided by Lewis Laboratory that solutions of $CdSO_4$ having a pH of about 2 should receive first consideration in the experimental program. There is a possibility of formation of reduced solute and of scavenger action with this solution. The proposed experimental program for this solution is the following:

A. Design and develop equipment and procedures for investigating

the steady-state gas pressure and the solution stability during exposure in the LITR. An important part of this development will be measurement of the rates of energy deposition in H_2O of neutrons and γ-rays and their adjustment to a ratio near that which will prevail in the TWMR (two neutrons to one γ-ray).

The gas pressure experiments will be of the autoclave type. Equipment and procedures will be included for expelling and collecting the solution, and for analyzing the collected solution at a convenient time. Facilities will also be included for determining $(H_2)_{ss}$ during or shortly after irradiation by some method yet to be developed. As discussed previously, the bubble formation-pressure method is considered promising and this method will be tried first. It is expected that in-pile experiments with H_2O, D_2O, and possibly other solutions in which the steady-state concentrations are known, will be required in the development and testing of the bubble formation method (or alternative method). It is not anticipated that forced convection will be required to control temperature in LITR experiments. The autoclaves will be constructed of Zircaloy-2.

The experiments for determining solution stability will also be of the autoclave type. Equipment and procedures will be provided for expelling the solution through a filter and analyzing the separated solutions. Area to solution volume ratios will be one of the controlled experimental parameters.

B. Design and develop equipment for determining the stability of solutions during exposure to Van de Graaff electrons at dose rates up to 150 w/cc. These experiments will also be of an autoclave type. Equipment

and procedures will be provided for expelling the solution through a filter during irradiation and analyzing the separated solutions. As part of the development work for experiments, it will be necessary to design equipment and techniques which will enable adequate temperature control at the high radiation power densities which will be used. Thin layers of solution in contact with conducting surfaces, or stirring of somewhat thicker layers are possible approaches. The maximum volume of solution which can be employed is about 0.3 cc. Surface area to solution volume ratios will be one of the controlled parameters.

It will also be necessary to determine and, possibly, make provisions for controlling the uniformity of the electron current over the surface of the autoclave cell. The relationship between observed current and dose rate in the solution must also be determined.

C. Determine steady-stage concentrations in H_2O and D_2O in the LITR at (1) several concentrations of excess H_2 and D_2, for example, α-values of 0, -5×10^{-4}, -1×10^{-3}, -2×10^{-3}, and possibly lower, (2) at several concentrations of sulfuric acid, for example, pH 7, 5, 3, 2, and 1, and (3) at several temperatures, for example, 60, 75, 90, and 110°C.

D. Determine steady-state D_2 concentrations in the LITR for D_2O solutions of $CdSO_4$ at pH 2, α equal to zero, and temperatures of 60 to 90°C. Also confirm solution stability if indicated by Van de Graaff studies.

E. Determine solution stability under irradiation by Van de Graaff electrons at intensities up to 150 w/cc. Ranges of concentrations of excess H_2, pH and temperatures similar to those mentioned in (C) should

be tested. The Van de Graaff experiments will provide a severe test of solution stability. That is, instability is most likely to appear during electron irradiations.

F. The work which will follow will depend upon the results obtained; especially the results of D and E.

1. If the $(D_2)_{ss}$ observed in (D) is above about 2.3×10^{-2} M, it is very likely that the $(D_2)_{ss}$ in the same solutions and at the same temperature in the TWMR will exceed the tolerable limit of about 2.5×10^{-2} M. An increase in the (D^+) or addition of excess D_2 or both may reduce the $(D_2)_{ss}$ during irradiation to a level at which the solution may hold some promise for use in TWMR. The effects of such solution composition changes should be tested.

2. If the $(D_2)_{ss}$ is below 2.3×10^{-2} M, and the solution is stable, there is a possibility that the solution will prove useful in the TWMR. Additional experiments and considerations of experimental results, including the following, should then be carried out.

a. In-pile experiments to determine radiolysis under conditions of interest should be performed.

b. Employ results in computer calculations to determine the probable $(H_2)_{ss}$ at TWMR conditions, and the probable uncertainty in the extrapolated value. Possible values of rate constants for different reactions of the solute would be assumed in these calculations in order to estimate the uncertainty in the extrapolated value.

G. Depending upon the results obtained in (F), including the results of analyses of the data, it may be desirable to carry out additional in-pile experiments at higher intensities to provide for better extrapolation to TWMR fluxes; however, design of such experiments must depend

heavily on the experience and results obtained in the program described above. Temperature control will, of course, be more difficult in these higher power density experiments.

A similar procedure would be followed in the investigation of other poison-control solutions with the exception of those for which neither scavenger action nor appreciable reduce solute are believed possible. Acidified solutions of $Gd_2(SO_4)_3$ comprise the latter class. However, it is believed that stability experiments employing Van de Graaff irradiations would also be made with $Gd_2(SO_4)_3$ solutions in order to uncover unforeseen factors, if any. A few in-pile experiments with these solutions will also be required. Investigations with H_3BO_3 solutions would include experiments with solutions containing boron-11, but no boron-10, in order to determine scavenger action of H_3BO_3.

APPENDIX I

Derivation of Final Terms in Eqs. 5b and 1b

These terms were derived by equating rates of formation and disappearance of S^{+n} and $S^{+(n-1)}$ according to reactions 24 and 25. For example,

$$\frac{d(S^{+n})_{ss}}{dt} = 0 = k_{25}(OH)_{ss}(S^{+(n-1)})_{ss} - k_{24}(e^-_{aq})_{ss}(S^{+n})_{ss}$$

also

$$(S^{+(n-1)}) + (S^{+n}) = a$$

or

$$(S^{+n}) = a - (S^{+(n-1)})$$

then

$$k_{25}(OH)_{ss}(S^{+(n-1)})_{ss} = a\,k_{24}(e^-_{aq})_{ss} - k_{24}(e^-_{aq})_{ss}(S^{+(n-1)})_{ss}$$

and

$$(S^{+(n-1)})_{ss} = \frac{a\,k_{24}(e^-_{aq})_{ss}}{k_{24}(e^-_{aq})_{ss} + k_{25}(OH)_{ss}} \quad .$$

Now according to reaction 25, OH reacts with $S^{+(n-1)}$. The rate at which OH is lost in this reaction is just

$$k_{25}(OH)_{ss}(S^{+(n-1)})_{ss} = a\,k_{25}(OH)_{ss}\,\frac{k_{24}(e^-_{aq})_{ss}}{k_{24}(e^-_{aq})_{ss} + k_{25}(OH)_{ss}}$$

The term on the right is the final term in Eq. 1b on p. 4. The appropriate terms for the other equations on p. 4 are derived similarly.

References

1. J. C. Griess, G. H. Jenks, D. M. Eissenberg and E. G. Bohlmann, "An Evaluation of The Chemical Problems Associated with The Aqueous System in The Tungsten Water Moderated Reactor," ORNL-TM-913, August, 1964.

2. G. H. Jenks, "Effects of Reactor Operation on HFIR Coolant," ORNL Report, to be published.

3. C. J. Hochanadel, "Radiation Decomposition of Water Used as a Moderator or Coolant (Material for Reactor Handbook)," ORNL-CF-56-12-32, December, 1956.

4. J. A. Ghormley, "Lifetime of Intermediates in Water Subjected to Electron Irradiation," Radiation Research, 5, 247-251 (1956).

5. H. A. Schwarz, "A Determination of Some Rate Constants for Radical Processes in The Radiation Chemistry of Water," J. Phys. Chem., 66, 255-262 (1962).

6. A. O. Allen, C. J. Hochanadel, J. A. Ghormley, and T. W. Davis, "Decomposition of Water and Aqueous Solutions Under Mixed Fast Neutron and Gamma Radiation," J. Phys. Chem., 56, 575-586 (1952).

6a. A. O. Allen, T. W. Davis, G. V. Elmore, J. A. Ghormley, B. M. Haines, and C. J. Hochanadel, "Decomposition of Water and Aqueous Solutions Under Pile Radiation," ORNL-130, Oct. 1949.

7. D. M. Richardson, A. O. Allen, and J. W. Boyle, "Dosimetry of Reactor Radiations by Calorimetric Measurements," Proc.of First Geneva Conference, 14, 209-212 (1956).

8. J. K. Thomas, Sheffield Gordon, and E. J. Hart, "The Rates of Reaction of the Hydrated Electron in Aqueous Inorganic Solutions," J. Phys. Chem., $\underline{68}$, 1524-1527 (1964).

9. J. H. Baxendale, E. M. Fielden, and J. P. Keene, "Absolute Rate Constants for The Reactions of Some Metal Ions with the Hydrated Electron," Proc. Chem. Soc., August, 1963, pp 242-243.

10. E. J. Hart, "The Hydrated Electron", Science, $\underline{146}$, 24 (1964).

11. J. H. Baxendale and R. S. Dixon, "Some Unusual Reductions by the Hydrated Electron", Proc. Chem. Soc., May 1963, pp 148-149.

12. A. O. Allen, "Radiation Yields and Reactions in Dilute Inorganic Solutions," Radiation Research, Supplement 4 (1964) pp 54-67.

13. Sheffield Gordon, "Radiation Chemistry of the Aqueous Eu^{3+}-Eu^{2+} System," Abstracts of Papers Presented at the 148th Meeting of The American Chemical Society, held at Chicago, August 30-Sept. 4, 1964.

14. F. S. Dainton, "Chemical Effects of Radiation," Radiation Research, Supplement 1, 1-25 (1959).

15. H. A. Schwarz, "Intensity Effects, Pulsed Beam Effects, and the Current Status of Diffusion Kinetics," Radiation Research, Supplement 4, 1964, pp 89-109.

16. W. M. Latimer, Oxidation Potentials, Second Edition, Prentice-Hall, Inc., New York, 1952, p 295.

An Evaluation of The Chemical Problems
Associated With The Aqueous Systems in The
Tungsten Water Moderated Reactor, Addendum 2.

J. C. Griess

Corrosion of Hard-Coated Aluminum Specimen

Three hard-coated 6061-T6 aluminum specimens were subjected to test
in water and in a cadmium sulfate solution, and a fourth specimen was
sectioned to determine the thickness of the coating. The specimens were
supplied by Mr. H. W. Davison. The manner in which the specimens were
coated was not specified except that an anodizing procedure was used.
The initial film thickness on the specimen that was sectioned was 0.001
in., and the surface hardness was 357 diamond pyramid hardness (35 Rock-
well C).

The conditions of exposure and results were:

Environment	Temperature, $^{\circ}C$	Time, hr	Wt. Change, mg/cm^2
0.2M $CdSO_4$	150	1000	- 1.2
H_2O	30	1380	+ 0.1
H_2O	150	1500	+ 0.8

In all cases the specimens retained their original appearance and
no visible deposits were present on any of the surfaces. The specimen
exposed to the cadmium sulfate solution was treated with 8M HNO_3 at
60°C for 30 minutes after the first 50-hr exposure and again at the end
of the test to remove absorbed cadmium. Analysis of the nitric acid
solution indicated that after 50 hr the surface contained 12 μg of
cadmium/cm^2; at the end of the test, cadmium on the surface amounted to

39 $\mu g/cm^2$. It is probable that the two nitric acid treatments of the specimen accounted for at least some of the weight loss observed at the end of the test.

Similar tests in which untreated aluminum specimens were exposed to 0.2M $CdSO_4$ at 150°C showed heavy corrosion of the aluminum accompanied by the deposition of large amounts of metallic cadmium on the surface of the aluminum.[1] The hard-coat on the aluminum, therefore, was very beneficial in protecting the aluminum. It is highly improbable, however, that a system as complex as the poison-control system of the TWMR could be coated completely after assembly by such a process. Any uncoated areas or regions where cracks or defects in the coating occur would be subject to attack.

---

[1]J. C. Griess, G. H. Jenks, D. M. Eissenberg, and E. G. Bohlmann, "An Evaluation of the Chemical Problems Associated with the Aqueous System in the Tungsten Water Moderated Reactor," ORNL-TM-913, August 1964.

Table 1. Simultaneous Equations at Steady State and Reactions Involved

1. $0 = B + k_9(e_{aq}^-)(H_2O_2) - k_{12}(H_2)(OH) - k_{14}(OH)(H_2O_2) - k_{18}(OH)(HO_2) - 2k_{20}(OH)^2 + k_{21}(H_2O_2)(H) + k_{15}(H_2O_2)(HO_2) - k_{27}(OH)(e_{aq}^-) - k_{29}(OH)(H)$

2. $0 = C + k_{16b}(HO_2)^2 + k_{23}(e_{aq}^-)(HO_2) + k_{20}(OH)^2 - k_9(H_2O_2)(e_{aq}^-) - k_{14}(OH)(H_2O_2) - k_{15}(HO_2)(H_2O_2) - k_{21}(H_2O_2)(H)$

3. $0 = k_{15}(H_2O_2)(HO_2) + k_{16b}(HO_2)^2 + k_{18}(OH)(HO_2) - k_8(e_{aq}^-)(O_2) - k_{11}(H)(O_2)$

4. $0 = L + k_8(e_{aq}^-)(O_2) + k_{11}(H)(O_2) + k_{14}(OH)(H_2O_2) - k_{15}(H_2O_2)(HO_2) - 2k_{16b}(HO_2)^2 - k_{18}(OH)(HO_2) - k_{23}(H)(HO_2)$

5. $0 = F - k_8(e_{aq}^-)(O_2) - k_9(H_2O_2)(e_{aq}^-) - k_{22}(H^+)(e_{aq}^-) - 2k_{26}(e_{aq}^-)^2 - k_{27}(OH)(e_{aq}^-) - k_{30}(H)(e_{aq}^-)$

6. $0 = A - k_{12}(H_2)(OH) + k_{28}(H)^2 + k_{26}(e_{aq}^-)^2 + k_{30}(H)(e_{aq}^-)$

7. $0 = (H_2) + \alpha - (H_2O_2) - 2(O_2) - 1.5(HO_2)$

8. $0 = k_{12}(OH)(H_2) + k_{22}(H^+)(e_{aq}^-) - k_{11}(H)(O_2) - k_{23}(H)(HO_2) - k_{21}(H)(H_2O_2) - 2k_{28}(H)^2 - k_{29}(H)(OH) - k_{30}(H)(e_{aq}^-)$

A, B, C, F, L - Rates of formation of H_2, OH, H_2O_2, e_{aq}^- and HO_2, respectively.

Reaction Number	Reaction
8	$e_{aq}^- + O_2 \to O_2^-$
9	$e_{aq}^- + H_2O_2 \to OH + OH^-$
11	$H + O_2 \to HO_2$
12	$H_2 + OH \to H + H_2O$
14	$H_2O_2 + OH \to HO_2 + H_2O$
15	$HO_2 + H_2O_2 \to OH + H_2O + O_2$
16	$2HO_2 \to H_2O_2 + O_2$
16b	$O_2^- + O_2^- \xrightarrow{2H_2O} H_2O_2 + O_2 + 2OH^-$
18	$OH + HO_2 \to H_2O + O_2$
18a	$OH + HO_2 \to H_2O_3$

Reaction Number	Reaction
20	$OH + OH \to H_2O_2$
21	$H + H_2O_2 \to H_2O + OH$
22	$e_{aq}^- + H^+ \to H$
23	$H + HO_2 \to H_2O_2$
26	$e_{aq}^- + e_{aq}^- \xrightarrow{2H_2O} H_2 + 2OH^-$
27	$e_{aq}^- + OH \to OH^-$
28	$H + H \to H_2$
29	$H + OH \to H_2O$
30	$e_{aq}^- + H \xrightarrow{H_2O} H_2 + OH^-$

Table 2. Rates of Production of Radiolytic Species Employed in Electron Irradiation Calculations

Rates of Production (M, ℓ^{-1}, sec^{-1}) at Listed Radiation Intensities (w/cc)

Species	150	125	100	75	50	25	10	2.5	0.5	0.1
H_2	6.90E-3	5.75E-3	4.60E-3	3.45E-3	2.30E-3	1.15E-3	4.60E-4	1.15E-4	2.30E-5	4.60E-6
OH	3.68E-2	3.07E-2	2.45E-2	1.84E-2	1.226E-3	6.13E-3	2.45E-3	6.13E-4	1.226E-4	2.45E-5
H_2O_2	1.09E-2	9.08E-3	7.27E-3	5.45E-3	3.64E-3	1.82E-3	7.27E-4	1.82E-4	3.64E-5	7.27E-6
e^-_{aq}	4.48E-2	3.736E-2	2.984E-2	2.24E-2	1.494E-2	7.47E-3	2.984E-3	7.47E-4	1.494E-4	2.984E-5
HO_2^*										
H^*										

*Rates of production of HO_2 and H assumed to be zero.

Table 3. Rates of Production of Radiolytic Species Employed in Reactor Irradiation Calculations

Rates of Production (M, ℓ^{-1}, sec) at Listed Intensity (w/cc)

Species	150	125	100	75	50	25	10	2.5	0.5
H_2	1.73E-2	1.44E-2	1.15E-2	8.65E-3	5.77E-3	2.88E-3	1.15E-3	2.88E-4	5.77E-5
OH	1.46E-2	1.21E-2	9.72E-3	7.30E-3	4.87E-3	2.43E-3	9.72E-4	2.43E-4	4.87E-5
H_2O_2	1.67E-2	1.40E-2	1.11E-2	8.35E-3	5.57E-3	2.78E-3	1.11E-3	2.78E-4	5.57E-5
e_{aq}^-	1.997E-2	1.679E-2	1.33E-2	9.985E-3	6.66E-3	3.325E-3	1.33E-3	3.325E-4	6.66E-5
HO_2	2.19E-3	1.83E-3	1.46E-3	1.095E-3	7.30E-4	3.65E-4	1.46E-4	3.65E-5	7.30E-6
H^*									

*Rate of Production of H assumed to be zero.

Table 4

Calculated Concentrations of Radiolytic Products in

H_2O with Varying Concentrations of H^+ and α, Reactor Radiation

Concentrations (M) at Listed Irradiation Intensity (w/cc), (H^+) and α (M)

Species	$\alpha = 0.0$, $(H^+) = 10^{-5}$								$\alpha = 0.0$, $(H^+) = 0.0$	$\alpha = -1\times10^{-4}$, $(H^+)=1\times10^{-5}$		$\alpha = -5\times10^{-4}$, $(H^+)=10^{-5}$		$\alpha = -1\times10^{-3}$, $(H^+)=10^{-5}$
	150	125	75	50	25	10	2.5	0.5	2.5	150	25	125	50	75
OH	2.76E-8	2.54E-8	1.94E-8	1.58E-8	1.11E-8	7.03E-9	3.49E-9	1.71E-9	3.58E-9	3.03E-8	1.63E-8	1.13E-7	4.90E-8	3.98E-8
H_2O_2	1.47E-3	1.33E-3	1.05E-3	8.61E-4	6.15E-4	3.94E-4	2.05E-4	8.71E-5	1.86E-4	1.26E-3	3.41E-4	4.75E-5	3.45E-5	3.75E-5
O_2	1.04E-4	9.51E-5	7.16E-5	5.72E-5	3.85E-5	2.21E-5	8.19E-6	1.56E-6	1.44E-5	8.44E-5	1.53E-5	1.52E-8	5.27E-9	3.35E-9
HO_2	1.07E-5	9.78E-6	7.58E-6	6.19E-6	4.36E-6	2.74E-6	1.34E-6	5.26E-7	1.39E-6	1.02E-5	3.44E-6	1.12E-7	6.07E-8	6.16E-8
H_2	1.70E-3	1.53E-3	1.20E-3	9.84E-4	6.99E-4	4.42E-4	2.23E-4	9.10E-5	2.17E-4	1.54E-3	4.77E-4	5.48E-4	5.34E-4	1.04E-3
e^-_{aq}	4.05E-10	3.76E-10	2.84E-10	2.30E-10	1.60E-10	9.93E-11	4.69E-11	2.04E-11	5.34E-11	4.75E-10	2.87E-10	8.19E-9	4.07E-9	5.76E-9
H	2.95E-9	2.69E-9	2.15E-9	1.79E-9	1.33E-9	9.28E-10	6.19E-10	5.81E-10	3.54E-10	3.58E-9	3.08E-9	4.97E-7	3.40E-7	4.41E-7
H_2O_2/OH	5.3E+4	5.2E+4	5.4E+4	5.4E+4	5.5E+4	5.6E+4	5.9E+4	5.1E+4	5.2E+4	4.2E+4	2.1E+4	4.2E+2	7.0E+2	9.0E+2
HO_2/OH	3.9E+2	3.9E+2	3.9E+2	3.9E+2	3.9E+2	3.9E+2	3.8E+2	3.1E+2	3.9E+2	3.4E+2	2.1E+2	1.0	1.2	1.5

Table 5. Calculated Concentrations of Radiolytic Products in Water Under Electron Irradiation

Species	Concentration (M) at Listed Irradiation Intensity (w/cc)										
	150*	100*	50*	10*	150**	100**	50**	10**	2.5**	0.5**	0.1**
OH	2.03E-7	1.55E-7	9.83E-8	3.27E-8	3.31E-7	2.69E-7	1.90E-7	8.49E-8	4.26E-8	1.91E-8	8.49E-9
H_2O_2	2.28E-5	2.05E-5	1.71E-5	1.21E-5	1.17E-5	9.64E-6	6.80E-6	3.05E-6	1.52E-6	6.80E-7	3.05E-7
O_2	3.06E-5	2.65E-5	2.05E-5	1.14E-5	2.00E-5	1.64E-5	1.16E-5	5.20E-6	2.59E-6	1.16E-6	5.20E-7
HO_2	5.18E-6	4.50E-6	3.52E-6	2.02E-6	3.20E-6	2.62E-6	1.85E-6	8.29E-7	4.13E-7	1.85E-7	8.29E-8
H_2	9.19E-5	8.02E-5	6.34E-5	3.80E-5	5.67E-5	4.66E-5	3.28E-5	1.47E-5	7.34E-6	3.28E-6	1.47E-6
e^-_{aq}	1.65E-8	1.22E-8	7.24E-9	2.01E-9	3.40E-8	2.76E-8	1.96E-8	8.72E-9	4.38E-9	1.96E-9	8.72E-10
H	9.10E-9	7.47E-9	5.36E-9	2.40E-9	5.91E-9	4.80E-9	3.41E-9	1.52E-9	7.61E-10	3.41E-10	1.52E-10
H_2O_2/O_2	1.1E+2	1.3E+2	1.7E+2	3.7E+2							

$$*\quad \begin{cases} (H^+) = 1 \times 10^{-5}\ M \\ \alpha = 0.0\ M \end{cases}$$

$$**\quad \begin{cases} (H^+) = 0.0 \\ \alpha = 0.0 \end{cases}$$

Table 6. Reaction of Probable Importance in Radiolysis
of Poison-Control Solution

Reaction Number	Type	Reaction	Rate Constant at or near 25°C $(\sec^{-1}, M^{-1}, \ell)$	Assumed Activation Energy (Kcal, M^{-1})
	Reducing			
31		$Sm^{+3} + e^-_{aq} \longrightarrow SmII$	2.5×10^{10} [a]	3
32		$Gd^{+3} + e^-_{aq} \longrightarrow GdII$	5.5×10^8 [a]	4.5
33		$Cd^{+2} + e^-_{aq} \dashrightarrow CdI$	5.8×10^{10} [b]	3
34		$H_3BO_3 + e^-_{aq} \longrightarrow H_2BO_3^- + H$	---	---
	Oxidizing			
25	Scavenger	$S^{+(n-1)} + OH \longrightarrow S^{+n} + OH^-$	---	---
	Comparison	$Fe^{+2} + OH \longrightarrow Fe^{+3} + OH^-$	2.9×10^8 [c]	---
	Comparison	$EuII + OH \longrightarrow Eu^{+3} + OH^-$	3.8×10^9 [d]	---
	Comparison	$Sn^{+2} + OH \longrightarrow SmIII + OH^-$	2×10^9 [c]	---
35	Scavenger	$S^{+(n-1)} + H \longrightarrow S^{+n} + H_2$	---	---
	Comparison	$Fe^{+2} + H \xrightarrow{H^+} FeIII + H_2$	1.6×10^7 [c]	---
36	Non-scavenger	$S^{+(n-1)} + H_2O_2 \longrightarrow S^{+n} + OH + OH^-$	---	---
	Comparison	$Fe^{+2} + H_2O_2 \longrightarrow Fe^{+3} + OH + OH^-$	56 [e]	---
	Comparison	$Fe^{+2} + D_2O_2 \longrightarrow Fe^{+3} + OD + OD^-$	21 [e]	---
37	Non-Scavenger	$S^{+(n-1)} + HO_2 \xrightarrow{H^+} S^{+n} + H_2O_2$	---	---
	Comparison	$Fe^{+2} + HO_2 \xrightarrow{H^+} Fe^{+3} + H_2O_2$	slow [f]	
	Non-Scavenger	$S^{+(n-1)} + H^+ \longrightarrow S^{+n} + H$	---	---
	H_2SO_4 Reactions			
39		$HSO_4^- + OH \longrightarrow HSO_4 + OH^-$	2.1×10^5 [c]	10
40	Scavenger	$HSO_4 + e^-_{aq} \longrightarrow HSO_4^-$	---	---
41	Scavenger	$HSO_4 + H \longrightarrow HSO_4^- + H^+$	---	---
42	Scavenger	$HSO_4 + S^{+(n-1)} \longrightarrow HSO_4^- + S^{+n}$	---	---

[a]Ref. 8 [d]Ref. 13
[b]Ref. 9 [e]Ref. 14
[c]Ref. 12 [f]Ref. 15

Table 7. Additional Reactions of Possible Importance in Radiolysis
of Poison Control Solutions

Number	Reaction
43	$Sm^{+3} + H \longrightarrow Sm\ II + H^+$
44	$S^{+(n-1)} + O_2 \longrightarrow S^{+n} + HO_2^- + OH^-$
45	$Sm\ II + e_{aq}^- \longrightarrow Sm\ I$
46	$Sm\ I + Sm\ II \longrightarrow Sm^0 + Sm^{+3}$
47	$Cd\ I + e_{aq}^- \longrightarrow Cd^0$
48	$Cd\ I + Cd\ I \longrightarrow Cd^0 + Cd^{+2}$
49	$H_3BO_3 + OH \longrightarrow$?

Table 8. Calculated Concentrations of Radiolytic Products in Scavenger Solutions at Several Intensities and Concentrations of Excess H_2, Reactor Radiations

Species	Concentration (M) for $\alpha = 0.0$ and Listed Radiation Intensities (w/cc)					Concentration (M) for $\alpha = -1 \times 10^{-3}$ and Listed Radiation Intensities (w/cc)			
	150	75	10	2.5	0.5	125	75	25	2.5
OH	1.33E-8	7.94E-9	1.56E-9	4.65E-10	1.11E-10	3.71E-8	2.34E-8	8.41E-9	9.02E-10
H_2O_2	3.60E-3	3.08E-3	2.18E-3	1.85E-3	1.51E-3	4.14E-4	3.58E-4	2.78E-4	2.08E-4
O_2	9.33E-5	6.94E-5	4.18E-5	4.35E-5	7.31E-5	1.63E-7	1.09E-7	5.58E-8	3.62E-8
HO_2	1.16E-5	8.33E-6	3.20E-6	1.65E-6	7.43E-7	7.94E-7	6.12E-7	3.91E-7	2.30E-7
H_2	3.51E-3	2.94E-3	1.99E-3	1.67E-3	1.40E-3	1.08E-3	1.03E-3	9.42E-4	8.66E-4
e_{aq}^-	1.51E-10	8.61E-11	1.50E-11	4.17E-12	9.31E-13	5.86E-10	3.70E-10	1.37E-10	1.53E-10
H	2.98E-9	1.97E-9	4.42E-10	1.13E-10	1.48E-11	1.15E-7	8.48E-8	4.00E-8	5.84E-9
S^{+n}	4.1E-4	4.2E-4	4.5E-4	4.7E-4	4.8E-4	3.3E-4	3.3E-4	3.3E-4	3.2E-4
$S^{+(n-1)}$	5.9E-4	5.8E-4	5.5E-4	5.3E-4	5.2E-4	6.7E-4	6.7E-4	6.7E-4	6.8E-4
H_2O_2/OH	2.7E+5	3.9E+5	1.4E+6	4.0E+6	1.4E+7	1.1E+4	1.5E+4	3.3E+4	2.3E+5
HO_2/OH	8.7E+2	1.0E+3	2.1E+3	3.5E+3	6.7E+3	2.1E+1	2.6E+1	4.6E+1	2.5E+2

Case 1

$a = 0.001$ M

$k_{24} = 4.7 \times 10^{10}$

$k_{25} = 3.7 \times 10^8$

Table 9

Calculated Concentrations of Radiolytic Products in

Scavenger Solutions at Several Intensities and Concentrations

of Excess H_2, Reactor Radiations

Species	Concentration (M) for $\alpha = 0.0$ and Listed Radiation Intensities (w/cc)					Concentration (M) for $\alpha = -1 \times 10^{-3}$ and Listed Radiation Intensities (w/cc)				Concentration (M) for $\alpha = -2 \times 10^{-3}$ and Listed Radiation Intensities (w/cc)		
	150	100	50	10	0.5	125	75	25	2.5	150	50	0.5
OH	9.88E-9	7.19E-9	4.10E-9	1.04E-9	7.01E-11	1.17E-8	7.77E-9	2.99E-9	3.56E-10	1.71E-8	5.83E-9	6.03E-11
H_2O_2	4.59E-3	4.21E-3	3.71E-3	2.92E-3	2.04E-3	2.30E-3	2.00E-3	1.60E-3	1.18E-3	7.81E-4	6.98E-4	5.93E-4
O_2	6.09E-5	5.25E-5	4.30E-5	3.54E-5	9.22E-5	7.53E-6	5.53E-6	3.72E-6	3.05E-6	1.50E-7	1.27E-7	5.73E-7
HO_2	1.10E-5	9.07E-6	6.53E-6	3.04E-6	6.98E-7	6.20E-6	4.75E-6	2.86E-6	1.06E-6	1.07E-6	8.60E-7	3.32E-7
H_2	4.73E-3	4.32E-3	3.80E-3	3.00E-3	2.23E-3	3.32E-3	3.01E-3	2.60E-3	2.19E-3	2.78E-3	2.69E-3	2.59E-3
e^-_{aq}	1.08E-10	7.67E-11	4.22E-11	9.94E-12	6.08E-13	1.47E-10	9.52E-11	3.58E-11	4.14E-12	2.94E-10	1.02E-10	1.07E-12
H	3.59E-9	3.03E-9	1.86E-9	4.76E-10	1.17E-11	1.32E-8	1.00E-8	4.72E-9	6.97E-10	8.53E-8	3.31E-8	3.85E-10
s^{+n}	2.0E-2	2.0E-2	2.0E-2	2.0E-2	2.0E-2	2.0E-2	2.0E-2	2.0E-2	2.0E-2	2.0E-2	2.0E-2	2.0E-2
$s^{+(n-1)}$	1.1E-5	1.1E-5	1.1E-5	1.0E-5	8.7E-6	1.3E-5	1.3E-5	1.2E-5	1.2E-5	1.8E-5	1.8E-5	1.9E-5
H_2O_2/OH	4.6E+5	5.9E+5	9.0E+5	2.8E+6	2.9E+7	2.0E+5	2.6E+5	5.4E+5	3.3E+6	4.6E+4	1.2E+5	9.8E+6
HO_2/OH	1.1E+3	1.3E+3	1.6E+3	2.9E+3	1.0E+4	5.3E+2	6.1E+2	9.6E+2	3.0E+3	6.3E+10	1.5E+2	5.5E+3

Case 2

$a = 0.02$ M

$k_{24} = 2.2 \times 10^9$

$k_{24} = 4.7 \times 10^{10}$

Table 10. Calculated Concentrations of Radiolytic
Products in Scavenger Solution

Species	Concentration (M) for α = 0.0 and 125 w/cc
OH	5.05E-9
H_2O_2	7.61E-3
O_2	9.16E-5
HO_2	1.06E-5
H_2	7.71E-3
e^-_{aq}	5.06E-11
H	2.24E-9
S^{+n}	2.0E-2
$S^{+(n-1)}$	1.1E-4
H_2O_2/OH	1.5E+6
$HO_2 \cdot OH$	2.1E+3

Case 3

a $= 0.02$ M

$k_{24} = 5 \times 10^9$

$k_{25} = 5 \times 10^9$

Table 11. Calculated Concentrations of Radiolytic Products in Scavenger Solutions Under Electron Irradiation

Species	Concentration (M) at Listed Irradiation Intensity (w/cc)						
	0.1	0.5	2.5	10	50	100	150
OH	1.18E-10	5.36E-10	2.36E-9	8.12E-9	3.27E-8	5.89E-8	8.28E-8
H_2O_2	2.37E-4	2.51E-4	2.52E-4	2.45E-4	2.34E-4	2.30E-4	2.27E-4
O_2	5.59E-5	6.11E-5	7.83E-5	1.03E-4	1.42E-4	1.60E-4	1.72E-4
HO_2	2.73E-7	5.95E-7	1.24E-6	2.24E-6	4.22E-6	5.44E-6	6.26E-6
H_2	1.06E-4	1.16E-4	1.32E-4	1.53E-4	1.90E-4	2.11E-4	2.25E-4
e^-_{aq}	8.78E-13	4.49E-12	2.33E-11	9.72E-11	5.16E-10	1.05E-9	1.60E-9
H	1.81E-12	8.24E-12	3.22E-11	9.80E-11	3.57E-10	6.30E-10	8.82E-10
S^{+n}	5.1E-4	4.9E-4	4.4E-4	4.0E-4	3.3E-4	3.1E-4	2.9E-4
$S^{+(n-1)}$	4.9E-4	5.1E-4	5.6E-4	6.0E-4	6.7E-4	6.9E-4	7.1E-4
H_2O_2/OH	2.0E+6	4.7E+5	1.1E+5	3.0E+5	7.2E+3	3.9E+3	2.7E+3
HO_2/OH	2.3E+3	1.1E+3	5.3E+2	2.8E+2	1.3E+2	9.2E+1	7.6E+1

Case 4

$a = 0.001$ M

$k_{24} = 4.7 \times 10^{10}$

$k_{25} = 3.7 \times 10^{8}$

Table 12. Calculated Concentrations of Radiolytic Products in
Scavenger Solutions Under Electron Irradiations

Species	Concentration (M) at Listed Radiation Intensities (w/cc)		
	150	50	0.5
OH	3.39E-8	1.39E-8	2.10E-10
H_2O_2	4.77E-4	4.32E-4	3.05E-4
O_2	3.75E-5	9.12E-6	1.32E-6
HO_2	5.25E-6	2.83E-6	3.49E-7
H_2	5.50E-4	4.46E-4	2.97E-4
e_{aq}^-	7.40E-10	2.57E-10	2.79E-12
H	3.32E-9	3.65E-9	1.79E-10
S^{+n}	2E-2	2E-2	2E-2
$S^{+(n-1)}$	2.0E-5	1.7E-5	1.2E-5
H_2O_2/OH	1.4E+4	3.1E+4	1.5E+6
HO_2/OH	1.6E+2	2.0E+2	1.7E+3

Case 5

$$a = 0.02 \text{ M}$$

$$k_{24} = 2.2 \times 10^9$$

$$k_{25} = 4.7 \times 10^{10}$$

$$\alpha = 0.0$$

$$(H^+) = 1 \times 10^{-5} \text{ M}$$

-61-

Table 13. Estimates of Changes in $(S^{+(n-1)})$ and (H_2) After Exposure to Reactor Radiations

I w/cc	F M, ℓ^{-1}, sec^{-1}	Assumed Value of $(S^{+(n-1)})_{ss}$ M, ℓ^{-1}	Assumed Delay of Time sec	Calculated Change in $(S^{+(n-1)})$ M, ℓ^{-1}	Five Times* Calculated Change in $(S^{+(n-1)})$ M, ℓ^{-1}	Calculated Initial Concentration of H_2 M, ℓ^{-1}	Estimated Percentage Change in (H_2)
0.5	6.7×10^{-5}	10^{-4}	10^{-2}	6.7×10^{-7}	3.4×10^{-6}	9×10^{-5}	3.8
		10^{-4}	10^{-1}	6.7×10^{-6}	3.4×10^{-5}	9×10^{-5}	38
		10^{-3}	10^{-2}	6.7×10^{-7}	3.4×10^{-6}	9×10^{-5}	3.8
		10^{-3}	10^{-1}	6.7×10^{-6}	3.4×10^{-5}	9×10^{-5}	38
		10^{-4}	10^{-3}	6.7×10^{-8}	3.4×10^{-7}	9×10^{-5}	0.4
10	1.3×10^{-3}	10^{-4}	10^{-2}	1.2×10^{-5}	6.0×10^{-5}	4.4×10^{-4}	14
		10^{-4}	10^{-1}	7.3×10^{-5}	3.7×10^{-4}	4.4×10^{-4}	84
		10^{-3}	10^{-2}	1.3×10^{-5}	6.5×10^{-4}	4.4×10^{-4}	14
		10^{-4}	10^{-3}	1.3×10^{-6}	6.5×10^{-6}	4.4×10^{-4}	1.4
150	2.0×10^{-2}	10^{-4}	10^{-2}	8.6×10^{-5}	4.3×10^{-4}	4.4×10^{-4}	100
		10^{-3}	10^{-2}	1.8×10^{-4}	9×10^{-4}	4.4×10^{-4}	100

* Estimated possible change in (H_2).

Table 14. Estimates of Changes in $(S^{+(n-1)})$ and (H_2) After Exposure to Van de Graaff Electrons

I w/cc	F M, ℓ⁻¹, sec⁻¹	Assumed Value of $(S^{+(n-1)})_{ss}$ M, ℓ⁻¹	Assumed Delay of Time sec	Calculated Change in $(S^{+(n-1)})$ M, ℓ⁻¹	Five Times* Calculated Change in $(S^{+(n-1)})$ M, ℓ⁻¹	Calculated Initial Concentration of H_2 M, ℓ⁻¹	Estimated Percentage Change in (H_2)
0.5	1.4×10^{-4}	10^{-4}	10^{-2}	1.5×10^{-6}	7.5×10^{-6}	3×10^{-6}	100
		10^{-4}	10^{-3}	1.5×10^{-7}	7.5×10^{-7}	3×10^{-6}	25
		10^{-4}	10^{-4}	1.5×10^{-8}	7.5×10^{-8}	3×10^{-6}	2.5
		10^{-3}	10^{-3}	1.5×10^{-7}	7.5×10^{-7}	3×10^{-6}	25
50	1.5×10^{-2}	10^{-4}	10^{-3}	1.5×10^{-5}	7.5×10^{-5}	3.3×10^{-5}	100
		10^{-4}	10^{-4}	1.5×10^{-6}	7.5×10^{-6}	3.3×10^{-5}	23
150	4.5×10^{-2}	10^{-4}	10^{-4}	4.5×10^{-6}	2.3×10^{-5}	5.7×10^{-5}	40
		10^{-4}	5×10^{-4}	2.0×10^{-5}	1.0×10^{-4}	5.7×10^{-5}	100

* Estimated possible change in (H_2).

Table 15

Summary of Proposed Experimental Program to
Evaluate Solution Stability and Gas Pressure Generation
During Irradiation in TWMR Poison-Control Solutions

| Source of Radiation		LITR	Higher Flux Reactor	Van de Graaff
Solution Stability	Priority	Necessary for all solutions	Not necessary	Necessary for all solutions
	Measurements	Expel solution through filter and analyze separated samples	------	Expel solution through filter and analyze separated samples
	Environmental Parameters	Ratio of neutron to γ-ray energy deposition rates Neutron energy spectrum Temperature Ratio of surface area to solution volume Concentration of Excess H_2 pH	------	Dose rate Temperature Ratio of surface area to solution volume Concentration of Excess H_2 pH
	Application of information	Check of Van de Graaff results		Possible elimination of a solution. Conservative value at all intensities
Gas Generation	Priority	Necessary for all solutions; also, H_2O, D_2O and solutions of H_3BO_3 containing only boron-11	Likely to be necessary depending upon results of LITR experiments, computer calculations employing LITR results and whether Van de Graaff experiments are performed	Likely to be necessary depending upon results of LITR experiments, computer calculations employing LITR results and whether Higher Flux Reactor experiments are performed
	Measurements	Solution analyses with solutions of acid $Gd_2(SO_4)_3$ and $CdSO_4$. Method to be developed for higher pH solutions of $Gd_2(SO_4)_3$ and $CdSO_4$ and for $Sm_2(SO_4)_3$ and H_3BO_3. The bubble formation method appears most promising. Methods other than solution analyses are likely to be most difficult with Van de Graaff.		
	Environmental Parameters	Ratio of neutron to γ-ray energy deposition rates Neutron energy spectrum Temperature Concentration of excess H_2 pH		Dose rate Temperature Concentration of excess H_2 pH
	Application of information	Possible elimination of a solution Calculation check point Better understanding of radiolytic behavior	Possible elimination of a solution Calculation check point Extrapolation aid	Possible elimination of a solution Extrapolation aid
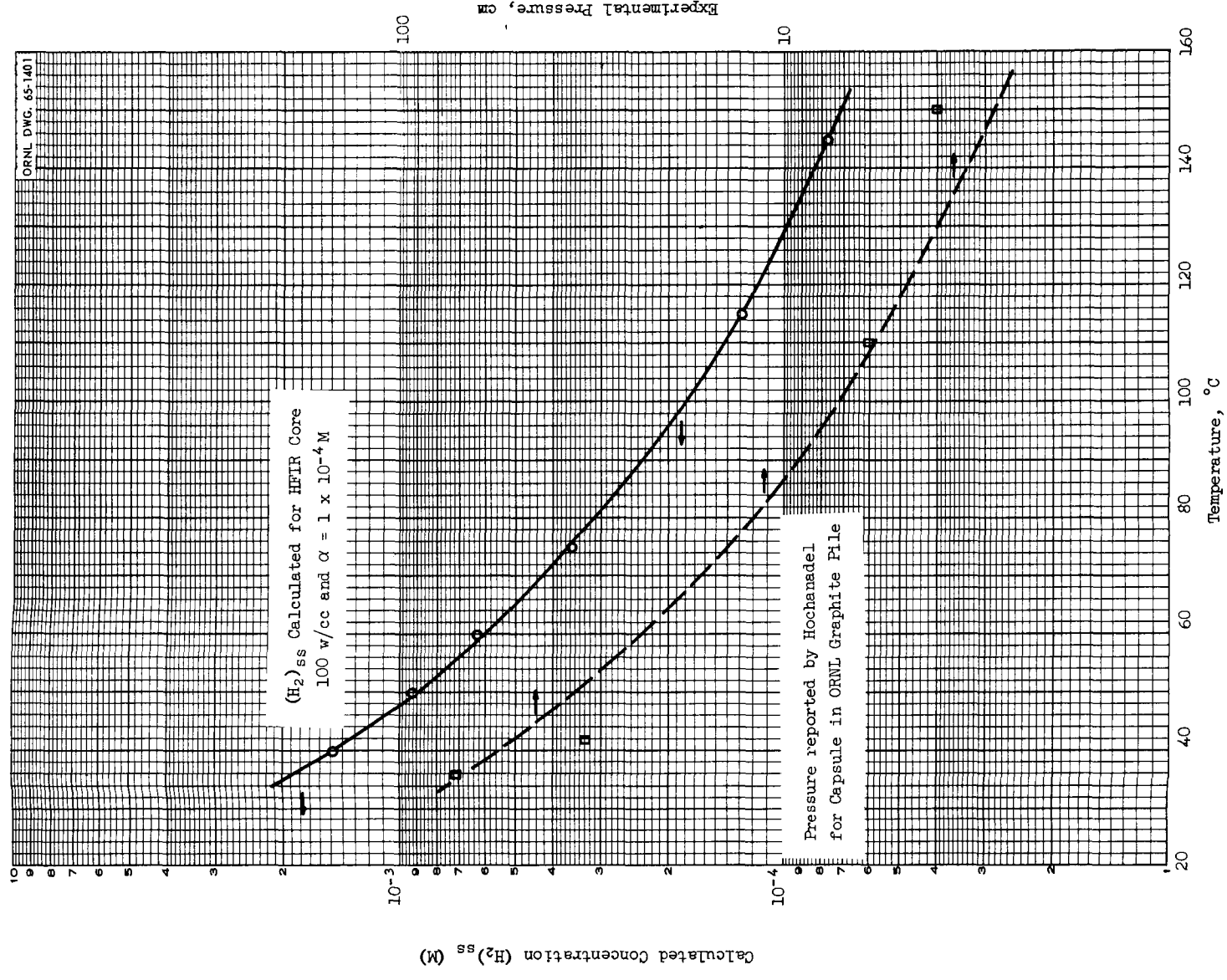
Figure 1. Variation of Calculated and Experimental Concentrations or Pressures with Temperature.
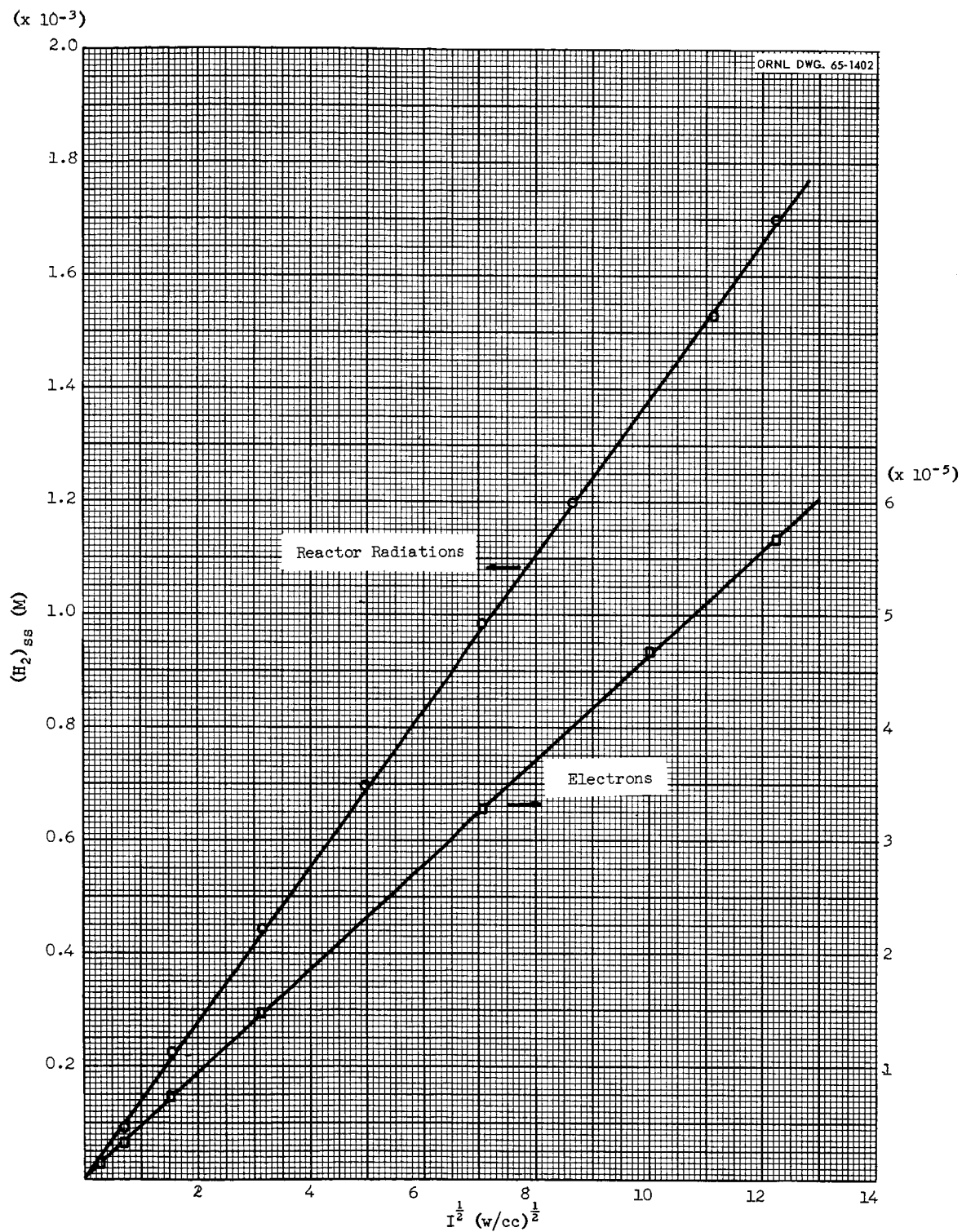
Figure 2. Calculated $(H_2)_{ss}$ in Water Under Exposure to Reactor Radiations and to Electrons.
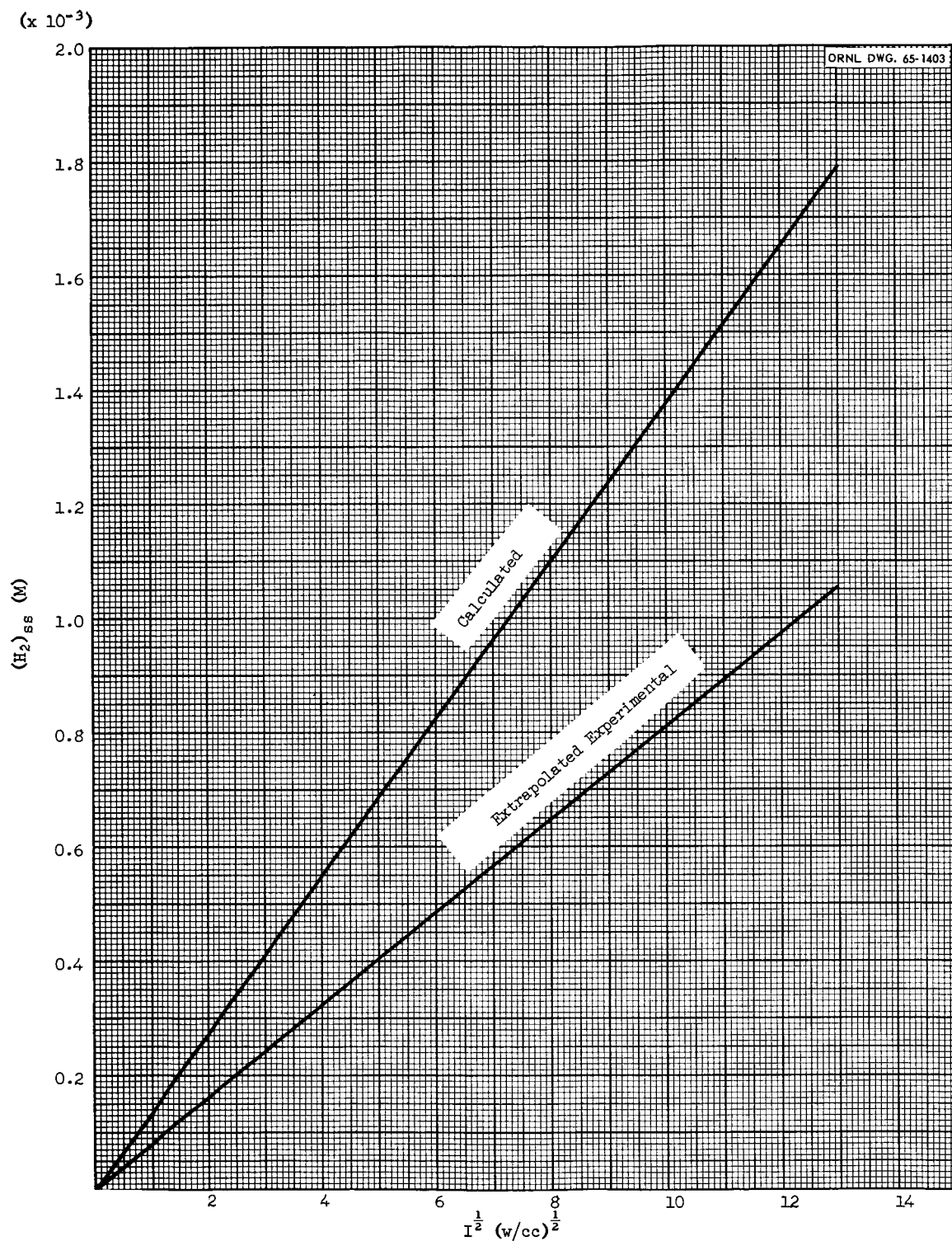
Figure 3. Comparison Between Calculated and Extrapolated
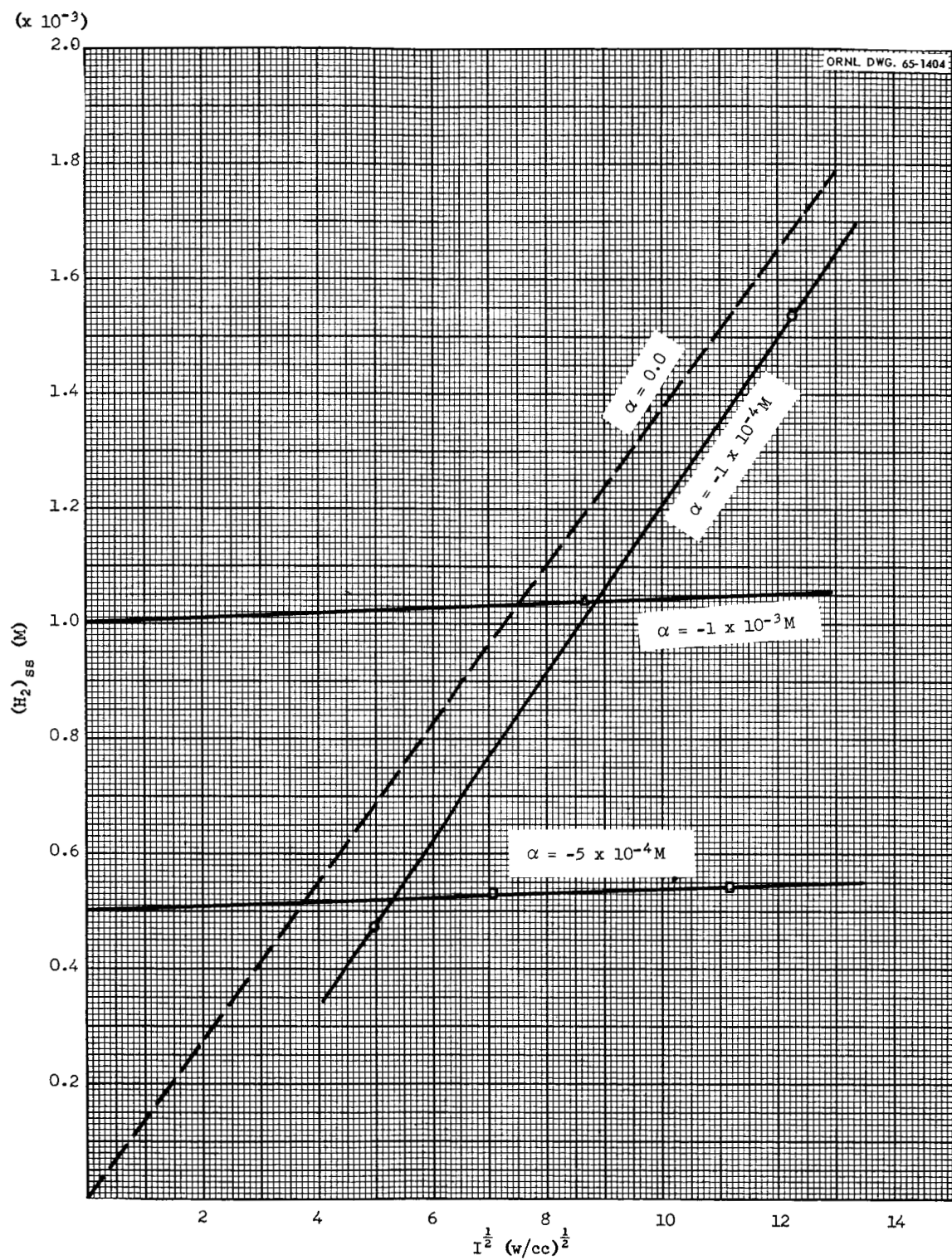Experimental Values of $(H_2)_{ss}$ in Water Exposed to Reactor Radiations.

Figure 4. Calculated $(H_2)_{SS}$ in H_2O with Varying Amounts of
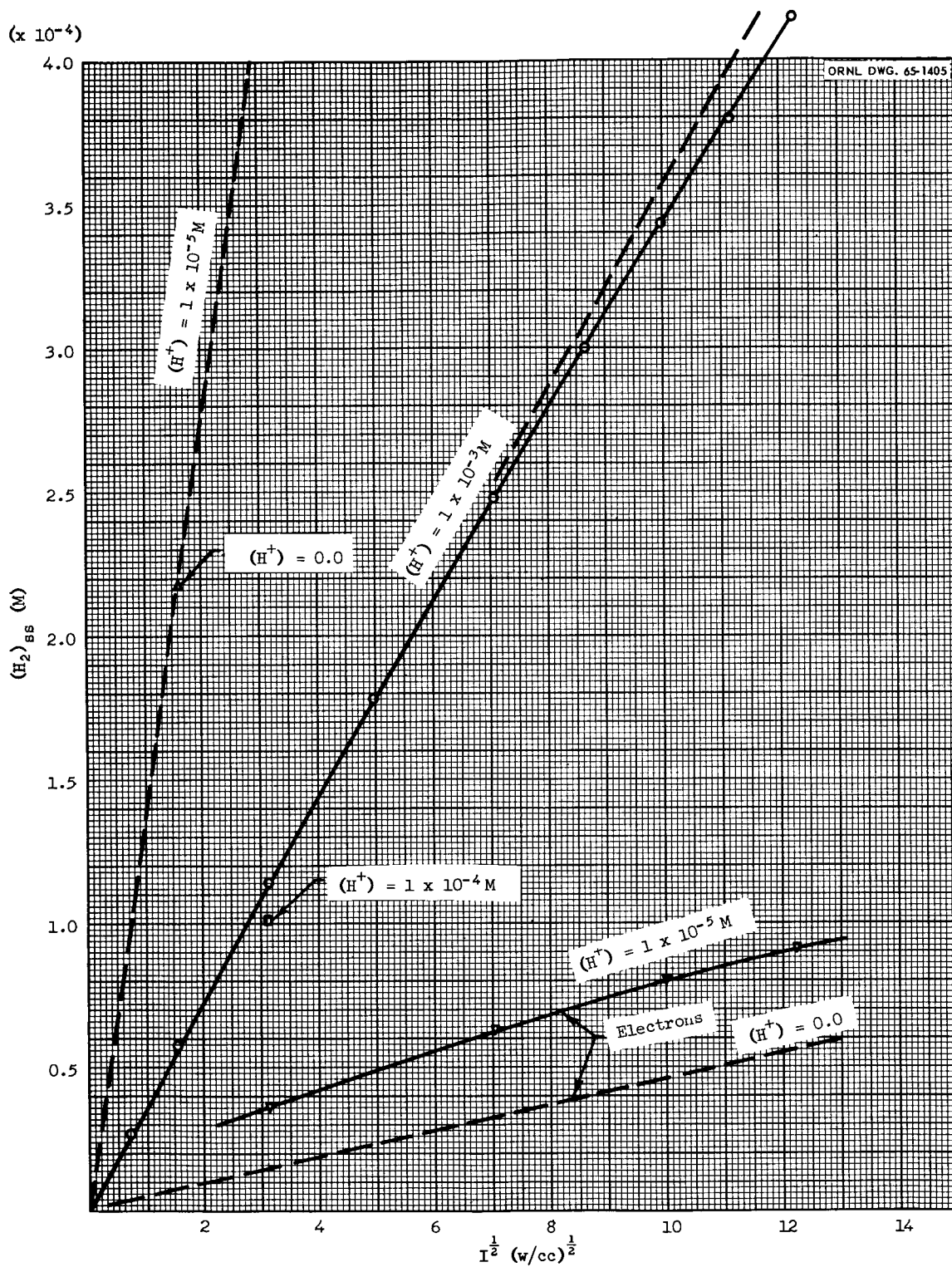Excess H_2. Reactor Radiations (Hydrogen Ion Concentration - 10^{-5} M).

Figure 5. Calculated $(H_2)_{ss}$ in H_2O with Varying (H^+). Reactor Radiations Unless Otherwise Noted.
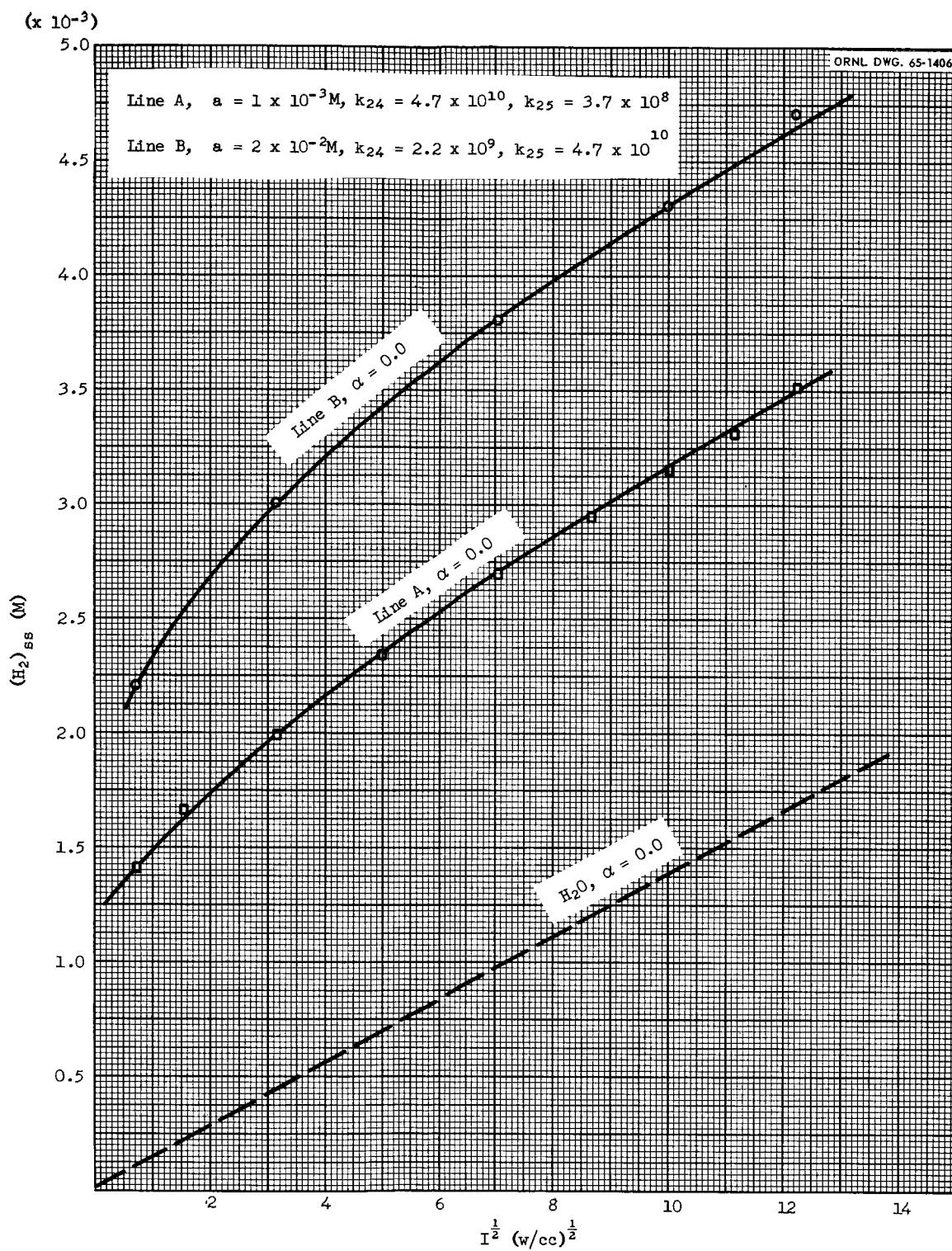
Figure 6. Calculated $(H_2)_{ss}$ in Cation Scavenger Solutions
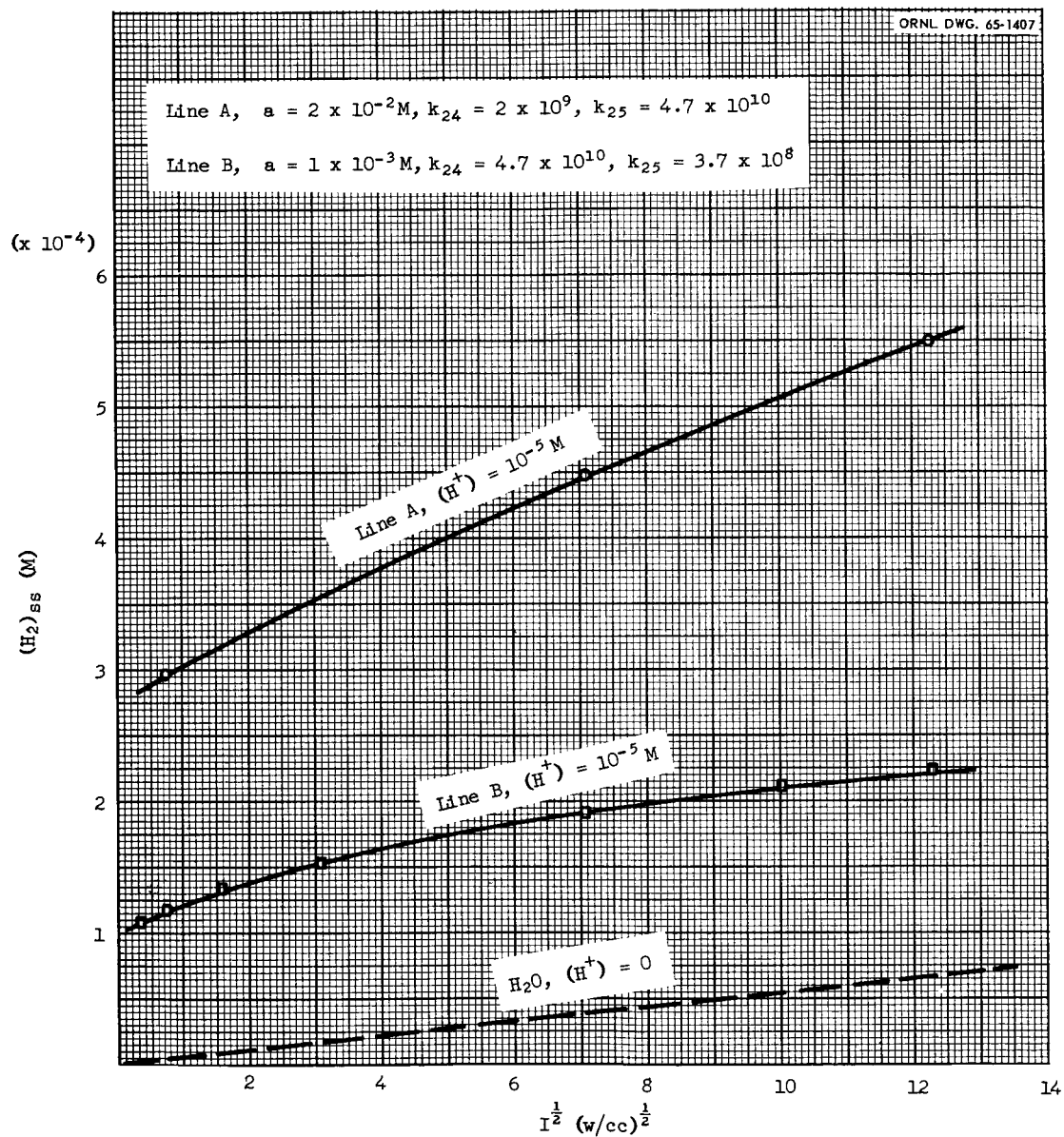
Figure 7. Calculated $(H_2)_{ss}$ in Scavenger Solutions and in Water Under Electron Irradiation.
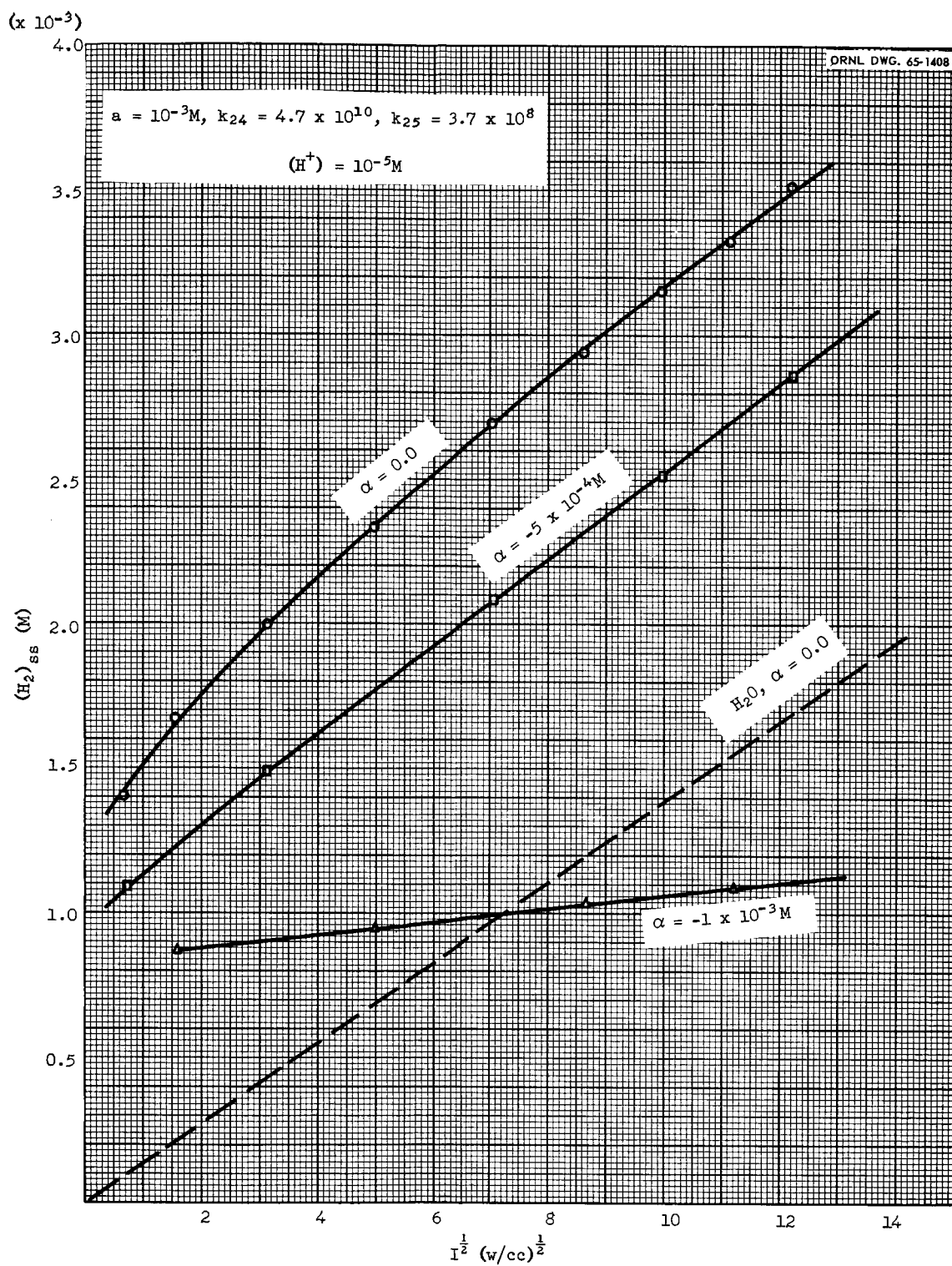
Figure 8. Calculated $(H_2)_{ss}$ in Scavenger Solution with Varying Amount of Excess H_2.
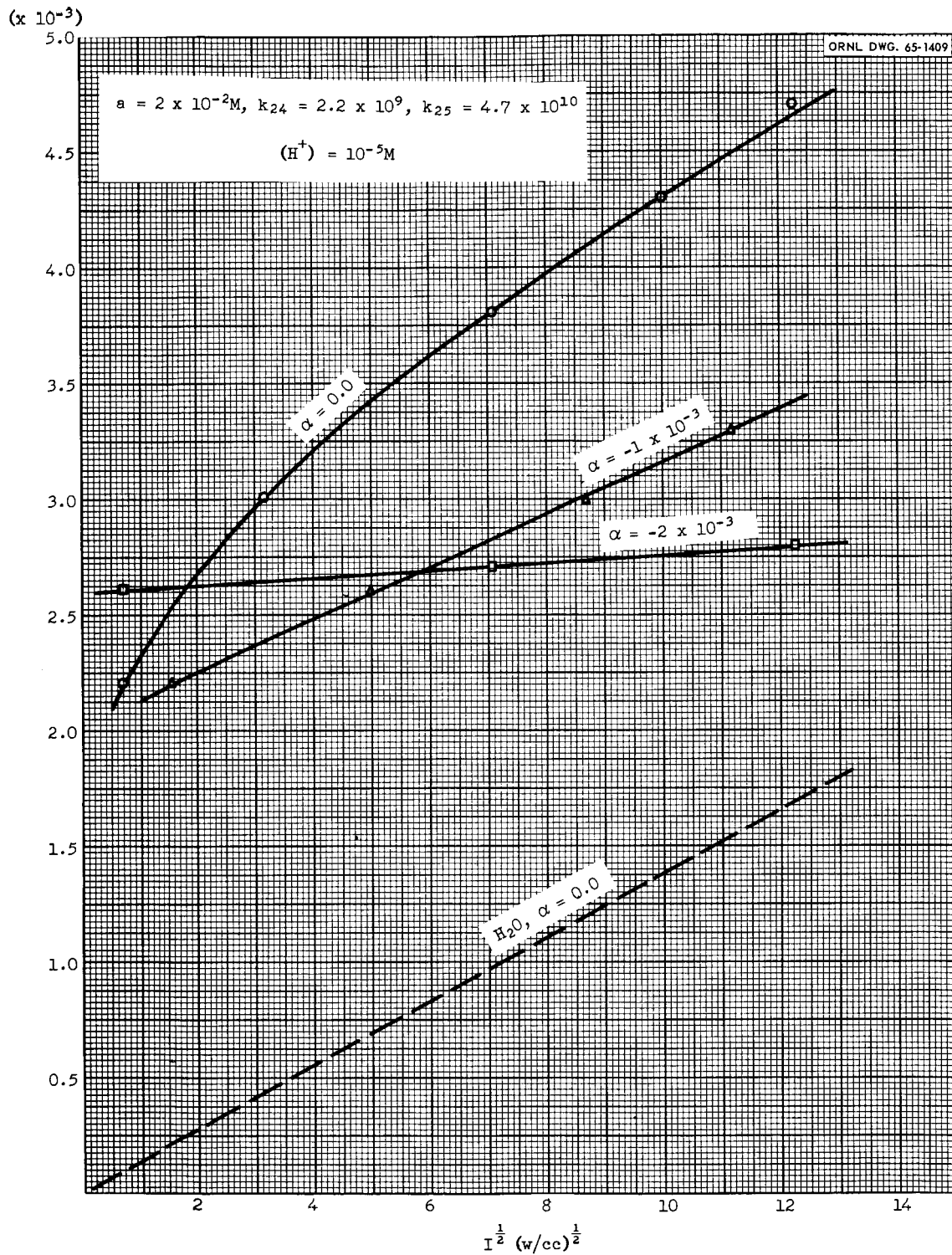
Figure 9. Calculated $(H_2)_{ss}$ in Scavenger Solutions with Varying Amount of Excess H_2.

List of Figures

Internal Distribution

1. S. E. Beall
2. E. G. Bohlmann
3. C. J. Borkowski
4. G. E. Boyd
5. E. L. Compere
6. D. M. Eissenberg
7. E. P. Epler
8. A. P. Fraas
9. J. H. Frye, Jr.
10-14. J. C. Griess
15. W. R. Grimes
16. C. J. Hochanadel
17. G. H. Jenks
18. J. A. Lane
19. C. E. Larson
20. H. G. MacPherson
21. W. L. Marshall
22. H. F. McDuffie
23-24. A. J. Miller
25. H. C. Savage
26. M. J. Skinner
27. I. Spiewak
28. A. M. Weinberg
29-30. Central Research Library, Document Section
31. Y-12 Technical Library, Document Section
32-34. Laboratory Records Department
35. Laboratory Records Department (LRD-RC)
36. Reactor Division Library

External Distribution

37. S. G. English, U. S. Atomic Energy Commission,
    Washington 25, D. C.
38. H. B. Finger, U. S. Atomic Energy Commission,
    Washington 25, D. C.
39. J. E. Morrissey, U. S. Atomic Energy Commission,
    Washington 25, D. C.
40. F. K. Pittman, U. S. Atomic Energy Commission,
    Washington 25, D. C.
41. L. V. Humble, NASA-Lewis Research Center
    21000 Brookpark Road, Cleveland, Ohio 44135
42. N. T. Musial, NASA-Lewis Research Center
    21000 Brookpark Road, Cleveland, Ohio 44135
43. S. J. Kaufman, NASA-Lewis Research Center
    21000 Brookpark Road, Cleveland, Ohio 44135
44. M. H. Krasner, NASA-Lewis Research Center
    21000 Brookpark Road, Cleveland, Ohio 44135

External Distribution

45. J. C. Liwosz, Jr.,NASA-Lewis Research Center
    21000 Brookpark Road, Cleveland, Ohio 44135
46-48. Harry Davison, NASA-Lewis Research Center
    21000 Brookpark Road, Cleveland, Ohio 44135
49-50. LIBRARY, NASA-Lewis Research Center
    21000 Brookpark Road, Cleveland, Ohio 44135
51. Report Control Office, NASA-Lewis Research Center
    21000 Brookpark Road, Cleveland, Ohio 44135

52-57. NASA Representative, NASA Scientific and Technical
    Information Facility
    Box 5700
    Bethesda, Maryland
58-60. U. S. Atomic Energy Commission
    Technical Reports Library
    Washington, D. C.

61-75. U. S. Atomic Energy Commission
    Technical Information Service Extension
    P. O. Box 62
    Oak Ridge, Tennessee

76-77. W. F. Eanes, Westinghouse Electric Corporation
    Atomic Power Division
    Box 355
    Pittsburgh, Pa.
78. Research and Development Division, ORO